

Syntheses and Properties of Salts of Chromophores with Ferrocenyl Electron Donor Groups and Quaternary Nitrogen Acceptors

Benjamin J. Coe,^{*,†} Rebecca J. Docherty,[†] Simon P. Foxon,[†] Elizabeth C. Harper,[†] Madeleine Helliwell,[†] James Raftery,[†] Koen Clays,[‡] Edith Franz,[‡] and Bruce S. Brunschwig[§]

[†]School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, U.K., [‡]Department of Chemistry, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium, and [§]Molecular Materials Research Center, Beckman Institute, MC 139-74, California Institute of Technology, 1200 East California Boulevard, Pasadena, California 91125

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A series of five new dipolar cations has been synthesized with ferrocenvl (Fc) electron donor groups *N*-arylpyridinium, *N*-methylquinolinium, N-methylbenzothiazolium, connected to or N-methylacridinium acceptors. Together with their known N-methylpyridinium analogue, these chromophores have been characterized as their PF_6^- salts by using various techniques including electronic absorption spectroscopy and cyclic voltammetry. Nine single-crystal X-ray structures have been determined, including two polymorphs of one salt obtained from a single crystallization experiment, and two of these are polar materials. A highly favorable degree of dipolar alignment for bulk NLO effects is observed in one case. Molecular quadratic nonlinear optical (NLO) responses have been determined by using femtosecond hyper-Rayleigh scattering (HRS) at 1300 nm and also via Stark (electroabsorption) spectroscopic studies on the intense $\pi \to \pi^*$ intraligand and $d \to \pi^*$ metal-to-ligand charge-transfer bands. A broad correlation between the electron acceptor strength and the HRS-derived first hyperpolarizabilities β and the static first hyperpolarizabilities β_0 estimated from the Stark data is evident. This is the first time that meaningful (albeit indirectly determined) β_0 data have been reported for Fc compounds, allowing quantitative comparisons with the chromophore in the technologically important material (E)-4'-(dimethylamino)-N-methyl-4-stilbazolium (DAS) tosylate. The observed β_0 values are in several cases similar to that of [DAS]PF₆, and possibly even larger in one instance.

Introduction

Organic nonlinear optical (NLO) materials have well-established relevance to various applications, such as optical data processing and biological imaging.¹ Although most work in this field has yet to make the transition to actual technological contexts, crystals of the organic salt (*E*)-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST; cation shown in Figure 1) have been commercialized recently for use in terahertz (THz) wave generation via nonlinear frequency mixing.² Many studies of a more fundamental nature have involved organotransition metal complexes; such compounds allow the ready combination of properties such as redox or magnetic behavior with desirable optical effects, offering the promise of innovative, multifunctional NLO materials.³

^{*}Address correspondence to this author. E-mail: b.coe@manchester. ac.uk.

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Figure 1. Structures of the new complexes 2-6 and the previously reported DAS, MFVP, and 1 cations.

For example, various reports of the use of reversible metalbased redox chemistry to switch different types of NLO properties have appeared over the past decade.⁴

Quadratic (second-order) NLO effects in molecules originate from the first hyperpolarizability, β , while cubic (third-order) phenomena result from the second hyperpolarizability, γ . Hyperpolarizability tensors relate to the response of molecular electronic charges to the applied oscillating electric field of a laser light beam, and the speed of response (essentially instantaneous) is one of the significant advantages of organic materials over the widely employed inorganic crystals that include lithium niobate (LiNbO₃) and potassium titanyl phosphate (KTiOPO₄).¹ The present investigation is focused on quadratic properties, which at the bulk level are most commonly represented by the phenomenon of second-harmonic generation (SHG) or frequency doubling. Electro-optic (EO) modulation is a related effect that also has considerable technological importance. The basic requirements for large β values in both purely organic and metal-containing chromophores are a relatively large, polarizable π -conjugated system with electron-donating and -accepting substituents.

Since a pioneering report by Green, Marder, and colleagues in 1987,⁵ a large number of quadratic NLO investigations have focused on using the ferrocenyl (Fc) group as an electron donor.^{3i,6} An Fc unit is attractive because it is relatively strongly electron-donating, is amenable to a vast range of functionalization chemistry, and shows very high stability. The literature also indicates that the presence of Fc units may serve to encourage the adoption of non-centrosymmetric crystal structures that are a requirement for bulk quadratic NLO activity. Recent demonstrations of redox-switching of β responses by exploiting the formally Fe^{III/II} couple^{4c,d,j} have further consolidated the promise of Fc-based donors for NLO studies. The only significant drawbacks of the Fc group are that its electrondonating power is limited (about the same as that of a 4-methoxyphenyl unit),⁷ and the presence of two low-energy intramolecular charge-transfer (ICT) transitions complicates the establishment of molecular structure-activity correlations. However, the octamethylferrocenyl unit is a considerably stronger donor than Fc itself.^{4c,d,j,6h,8} Studies of charged, Fc-containing NLO chromophores have included a number of monometallic species with mostly

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N-methylpyridinium electron acceptors^{7,9} and a range of bimetallic complexes.¹⁰ However, despite some very promising results, particularly with salts of the (*E*)-*N*-methyl-4-[2-(ferrocenyl)vinyl]pyridinium (MFVP) cation (Figure 1),^{9b} the potential of relatively simple salts containing Fc groups has not been explored thoroughly.

We have found previously that N-arylpyridinium units are especially strong electron acceptors that can lead to very large β values in metal-based and purely organic chromophores.11 The present report concerns NLO and other studies with a series of new Fc-containing chromophores that feature such acceptor groups as well as others, including the previously unexploited N-methylacridinium unit. Published reports have relied almost exclusively on the electric-field-induced SHG (EFISHG)¹² and hyper-Rayleigh scattering (HRS)¹³ techniques to measure β responses for metallocenyl chromophores, but such data cannot be used to derive realistic static (off-resonance) first hyperpolarizabilities β_0 for metallocenyl chromophores due to the presence of two relatively low-energy CT transitions that both contribute to the NLO response. Our application of Stark spectroscopy¹⁴ to determine β_0 values in this work therefore provides unique insights into the intrinsic NLO responses of representatives of this important class of compounds.

Experimental Section

Materials and Procedures. The compounds *N*-methyl-4-picolinium iodide ([Mepic⁺]I),¹⁵ *N*-phenyl-4-picolinium chloride hydrate ([Phpic⁺]Cl·1.25H₂O),¹⁶ *N*-(2-pyrimidyl)-4-picolinium

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hexafluorophosphate ([2-Pympic⁺]PF₆),¹⁶ 2,3-dimethylbenzothiazolium hexafluorophosphate ([dmbzt⁺]PF₆),¹⁷ *N*-methyl-4-methylquinolinium hexafluorophosphate ([Mequin⁺]PF₆),¹⁸ 9,10-dimethylacridinium iodide ([dmacd⁺]I),¹⁹ and 4-ferrocenylbenzaldehyde²⁰ were prepared according to literature procedures. All other reagents were obtained commercially and used as supplied. Products were dried at room temperature in a vacuum desiccator (CaSO₄) for ca. 24 h prior to characterization.

General Physical Measurements. ¹H NMR spectra were recorded on a Varian Unity 400 or a Bruker Ultrashield 500 spectrometer, and all chemical shifts are quoted with respect to TMS. The fine splitting of pyridyl or phenyl ring AA'BB' patterns is ignored, and the signals are reported as simple doublets, with the *J* values referring to the two most intense peaks. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester, and UV– visible spectra were obtained by using a Shimadzu UV-2401PC spectrophotometer. Mass spectra were recorded by using +electrospray with acetonitrile solutions on a Micromass Platform II spectrometer.

Cyclic voltammetric measurements were carried out with an EG&G PAR model 283 potentiostat/galvanostat. An EG&G PAR K0264 single-compartment microcell was used with a silver/silver chloride reference electrode (3 M NaCl, saturated AgCl) separated by a salt bridge from a 2 mm disk glassy carbon working electrode and Pt wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH₂), and [NBuⁿ₄]PF₆, purchased from Aldrich and used as supplied, was used as the supporting electrolyte. Solutions containing ca. 10^{-3} M analyte (0.1 M electrolyte) were deaerated by purging with N₂. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 200 mV s⁻¹.

Synthesis of (E)-4'-Ferrocenyl-N-methyl-4-stilbazolium Iodide, [1]I. 4-Ferrocenylbenzaldehyde (358 mg, 1.23 mmol) and [Mepic⁺]I (290 mg, 1.23 mmol) were dissolved in methanol (40 mL). Piperidine (5 drops) was added and the solution heated under reflux for 6 h in the dark before being allowed to cool to room temperature overnight. The red crystalline precipitate was filtered off, washed with diethyl ether, and dried: 357 mg, 55%; $\delta_{\rm H}$ (400 MHz, CD₃OD) 8.68 (2 H, d, J = 6.8 Hz, C₅H₄N), 8.15 $(2 \text{ H}, d, J = 6.8 \text{ Hz}, C_5 \text{H}_4 \text{N}), 7.92 (1 \text{ H}, d, J = 16.4 \text{ Hz}, \text{CH}),$ 7.68 (2 H, d, J = 8.0 Hz, C_6H_4), 7.61 (2 H, d, J = 8.8 Hz, C_6H_4), 7.41 (1 H, d, J = 16.4 Hz, CH), 4.81 (2 H, t, J = 2.0 Hz, C₅H₄), 4.43 (2 H, t, J = 2.0 Hz, C₅H₄), 4.30 (3 H, s, Me), 4.04 (5 H, s, C₅H₅). Anal. Calcd (%) for C₂₄H₂₂FeIN·H₂O: C, 54.88; H, 4.61; N, 2.67. Found: C, 54.96; H, 4.15; N, 2.67. Diffraction quality crystals were grown by vapor diffusion of diethyl ether into a methanol solution.

Synthesis of (*E*)-4'-Ferrocenyl-*N*-methyl-4-stilbazolium Hexafluorophosphate, [1]PF₆. To a solution of [1]I·H₂O (171 mg, 0.326 mmol) in a minimum of methanol was added aqueous NH₄PF₆. The red precipitate was filtered off, washed with water then diethyl ether, and dried: 137 mg, 80%; $\delta_{\rm H}$ (400 MHz, CD₃COCD₃) 8.90 (2 H, d, *J* = 6.8 Hz, C₅H₄N), 8.29 (2 H, d, *J* = 6.8 Hz, C₅H₄N), 8.02 (1 H, d, *J* = 16.4 Hz, CH), 7.71 (2 H, d, *J* = 8.4 Hz, C₆H₄), 7.66 (2 H, d, *J* = 8.4 Hz, C₆H₄), 7.54 (1 H, d, *J* = 16.0 Hz, CH), 4.86 (2 H, t, *J* = 2.0 Hz, C₅H₄), 4.50 (3 H, s, Me), 4.43 (2 H, t, *J* = 2.0 Hz, C₅H₄), 4.05 (5 H, s, C₅H₅). Anal. Calcd (%) for C₂₄H₂₂F₆FeNP: C, 54.88; H, 4.22; N, 2.67. Found: C, 54.67; H, 4.02; N, 2.65. *m*/*z* = 380 ([M - PF₆]⁺).

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Diffraction quality crystals were grown by vapor diffusion of diethyl ether into a DMF solution.

Synthesis of (*E*)-4'-Ferrocenyl-*N*-phenyl-4-stilbazolium Hexafluorophosphate, [2]PF₆. This compound was prepared in crude form in a manner similar to [1]PF₆ by using [Phpic⁺]Cl· 1.25H₂O (71 mg, 0.311 mmol) in place of [Mepic⁺]I, a reflux time of 4 h, and diethyl ether (250 mL). Purification was achieved by vapor diffusion of diethyl ether into an acetonitrile solution, affording diffraction quality deep red crystals: 119 mg, 65%; $\delta_{\rm H}$ (500 MHz, CD₃COCD₃) 9.18 (2 H, d, J =6.9 Hz, C₅H₄N), 8.46 (2 H, d, J = 7.0 Hz, C₅H₄N), 8.19 (1 H, d, J = 16.4 Hz, CH), 7.96–7.65 (5 H, CH and C₆H₄), 4.88 (2 H, t, J = 1.9 Hz, C₅H₄), 4.45 (2 H, t, J = 1.9 Hz, C₅H₄), 4.06 (5 H, s, C₅H₅). Anal. Calcd (%) for C₂₉H₂₄F₆FeNP: C, 59.31; H, 4.12; N, 2.38. Found: C, 59.40; H, 3.97; N, 2.43. m/z = 442 ([M – PF₆]⁺).

Synthesis of (E)-N-Methyl-4-[2-(4-ferrocenylphenyl)vinyl]quinolinium Hexafluorophosphate, [3]PF₆. This compound was prepared in a manner similar to [1]PF₆ by using [Mequin⁺]PF₆ (105 mg, 0.346 mmol) in place of [Mepic⁺]I to afford a purple solid that required no further purification: 94 mg, 47%; $\delta_{\rm H}$ (500 MHz, CD₃COCD₃) 9.37 (1 H, d, J = 6.7 Hz, C₉H₆N), 9.08 (1 H, d, J = 8.5 Hz, C₉H₆N), 8.58 (1 H, d, J = 8.8 Hz, C₉H₆N), 8.55 (1 H, d, J = 6.6 Hz, C₉H₆N), 8.40 (1 H, d, J = 15.8 Hz, CH), 8.35 (1 H, t, J = 7.6 Hz, C₉H₆N), 8.18 (1 H, d, J = 15.8 Hz, CH), 8.13 (1 H, t, J = 7.3 Hz, C₉H₆N), 7.90 (2 H, d, J = 8.2 Hz, C₆H₄), 7.71 (2 H, d, J = 8.6 Hz, C₆H₄), 4.89 (2 H, s, C₅H₄), 4.80 (3 H, s, Me), 4.46 (2 H, s, C₅H₄), 4.06 (5 H, s, C₅H₅). Anal. Calcd (%) for C₂₈H₂₄F₆FeNP: C, 58.46; H, 4.20; N, 2.43. Found: C, 58.32; H, 4.23; N, 2.38. m/z = 430 ([M – PF₆]⁺).

Synthesis of (E)-N-Methyl-2-[2-(4-ferrocenylphenyl)vinyl]benzothiazolium Hexafluorophosphate, [4]PF₆. This compound was prepared in a manner similar to [1]PF₆ by using [dmbzt⁺]PF₆ (107 mg, 0.346 mmol) in place of [Mepic⁺]I, ethanol (50 mL) in place of methanol, and N-methylmorpholine (7 drops) in place of piperidine, with a reflux time of 27 h. Precipitation with diethyl ether (250 mL) followed by reprecipitation from acetone/aqueous NH₄PF₆ afforded a black solid: 123 mg, 61%; $\delta_{\rm H}$ $(500 \text{ MHz}, \text{CD}_3\text{CN}) 8.20 (1 \text{ H}, \text{d}, J = 7.9 \text{ Hz}, \text{C}_6\text{H}_4), 8.08 (1 \text{ H}, \text{H}_2) = 7.9 \text{ Hz}, \text{C}_6\text{H}_4$ d, J = 15.8 Hz, CH), 8.03 (1 H, d, J = 8.5 Hz, C₆H₄), 7.87 (1 H, t, J = 7.3 Hz, C₆H₄), 7.82 (2 H, d, J = 8.6 Hz, C₆H₄-Fc), 7.78 $(1 \text{ H}, t, J = 7.3 \text{ Hz}, C_6 \text{H}_4)$ 7.70–7.64 (3 H, CH and $C_6 \text{H}_4$ –Fc), $4.86 (2 \text{ H}, \text{t}, J = 1.9 \text{ Hz}, \text{C}_5\text{H}_4), 4.49 (2 \text{ H}, \text{t}, J = 1.9 \text{ Hz}, \text{C}_5\text{H}_4),$ 4.23 (3 H, s, Me), 4.07 (5 H, s, C5H5). Anal. Calcd (%) for C₂₆H₂₂F₆FeNPS: C, 53.72; H, 3.81; N, 2.41. Found: C, 53.63; H, 3.61; N, 2.40. m/z = 436 ([M - PF₆]⁺). Diffraction quality crystals were grown by vapor diffusion of diethyl ether into an acetonitrile solution.

Synthesis of (*E*)-4'-Ferrocenyl-*N*-(2-pyrimidyl)-4-stilbazolium Hexafluorophosphate, [5]PF₆. This compound was prepared in a manner similar to [4]PF₆ by using [2-Pympic⁺]PF₆ (110 mg, 0.347 mmol) in place of [dmbzt⁺]PF₆ and a reaction time of 24 h. Reprecipitation from acetone/diethyl ether gave a purple solid: 60 mg, 30%; $\delta_{\rm H}$ (500 MHz, CD₃COCD₃) 10.00 (2 H, d, J = 7.0Hz, C₅H₄N), 9.22 (2 H, d, J = 4.7 Hz, C₄N₂H₃), 8.52 (2 H, d, J = 7.0 Hz, C₅H₄N), 8.30 (1 H, d, J = 16.1 Hz, CH), 7.96 (1 H, t, J = 4.4 Hz, C₄N₂H₃), 7.81 (2 H, d, J = 8.2 Hz, C₆H₄), 7.76–7.70 (3 H, CH and C₆H₄), 4.89 (2 H, s, C₅H₄), 4.47 (2 H, s, C₅H₄), 4.06 (5 H, s, C₅H₅). Anal. Calcd (%) for C₂₇H₂₂F₆FeN₃P: C, 55.03; H, 3.76; N, 7.13. Found: C, 55.29; H, 3.77; N, 6.98. m/z = 444 ([M – PF₆]⁺). Diffraction quality crystals were grown as for **4**.

Synthesis of (*E*)-*N*-Methyl-9-[2-(4-ferrocenylphenyl)vinyl]acridinium Hexafluorophosphate, [6]PF₆. This compound was prepared in a manner similar to [4]PF₆ by using 4-ferrocenylbenzaldehyde (200 mg, 0.689 mmol), [dmacd⁺]I (232 mg, 0.692 mmol) in place of [dmbzt⁺]PF₆, and a reaction time of 18 h to afford the crude product as a brown solid. This material was purified by using column chromatography on silica gel with dichloromethane/acetone (10:1) as eluant. The column separated two colored bands, green and brown. The brown band was collected, concentrated under reduced pressure, and dried to give a black solid: 47 mg, 11%; $\delta_{\rm H}$ (500 MHz, CD₃COCD₃) 9.02 (2 H, d, J = 8.8 Hz, C₁₃H₈N), 8.83 (2 H, d, J = 9.5 Hz, C₁₃H₈N), 8.62 (1 H, d, J = 16.4 Hz, CH), 8.51 (2 H, m, C₁₃H₈N), 8.06 (2 H, m, C₁₃H₈N), 7.92 (2 H, d, J = 8.6 Hz, C₆H₄), 7.75 (2 H, d, J = 8.2 Hz, C₆H₄), 7.46 (1 H, d, J = 16.1 Hz, CH), 5.03 (3 H, s, Me), 4.91 (2 H, t, J = 1.9 Hz, C₅H₄), 4.46 (2 H, t, J = 1.9 Hz, C₅H₄), 4.09 (5 H, s, C₅H₅). Anal. Calcd (%) for C₃₂H₂₆F₆FeNP: C, 61.46; H, 4.19; N, 2.24. Found: C, 61.18; H, 4.39; N, 2.27. m/z = 480 ([M – PF₆]⁺).

Synthesis of (*E*)-4'-Ferrocenyl-*N*-phenyl-4-stilbazolium Chloride, [2]Cl. [2]PF₆ (50 mg, 0.085 mmol) was dissolved in a minimum of acetone, and a concentrated solution of [NBuⁿ₄]Cl in acetone was added dropwise until a red precipitate formed. This solid was filtered off, washed with copious amounts of acetone, and dried: 37 mg, 87%; $\delta_{\rm H}$ (400 MHz, CD₃COD) 9.00 (2 H, d, J = 6.8 Hz, C₅H₄N), 8.31 (2 H, d, J = 6.8 Hz, C₅H₄N), 8.06 (1 H, d, J = 16.4 Hz, CH), 7.82–7.72 (7 H, C₆H₅ and C₆H₄), 7.64 (2 H, d, J =8.3 Hz, C₆H₄), 7.52 (1 H, d, J = 15.9 Hz, CH), 4.83 (2 H, s, C₅H₄), 4.45 (2 H, s, C₅H₄), 4.05 (5 H, s, C₅H₅). Anal. Calcd (%) for C₂₉H₂₄ClFeN·1.25H₂O: C, 69.62; H, 5.14; N, 2.80. Found: C, 69.52; H, 5.24; N, 2.71. Diffraction quality crystals were grown by vapor diffusion of diethyl ether into a methanol solution.

X-ray Crystallographic Studies. Data were collected on a Bruker APEX CCD X-ray diffractometer. Cryocooling to 100 K was carried out by using an Oxford Cryosystems 700 Series Cryostream Cooler. Intensity measurements were collected using graphite-monochromated MoK α radiation from a sealed X-ray tube with a monocapillary collimator. Data processing was carried out by using the Bruker SAINT²¹ software package, and semiempirical absorption corrections were applied by using SADABS.²¹ All of the structures were solved by direct methods and refined by full-matrix least-squares on all F_o^2 data using SHELXS-97²² and SHELXL-97,²³ respectively. All non-hydrogen atoms were refined anisotropically, except where there was disorder, with hydrogen atoms bonded to carbon included in calculated positions using the riding method. All other calculations were carried out by using the SHELXTL package.²⁴

In [1]PF₆, there are two anions and cations in the asymmetric unit. The ethylenyl atoms of one complex, C12 and C13, are disordered over two sites, the occupancies of which were constrained to sum to unity; the same type of disorder is present for atoms C17 and C18 in the complex in [1]I. For [1]PF₆·DMF, both the PF_6^- anion and DMF solvent were modeled for disorder. Although the data seemed reasonable, the R factors are quite high. The crystals showed no sign of twinning, so some loss of the included DMF may be occurring. In $[1][PF_6]_{0.5}[I]_{0.5}$, the asymmetric unit contains four complex cations, two PF_6^- and two I⁻ anions. One of the cyclopentadienyl rings has been constrained to be a regular pentagon. The crystal was twinned with twin law (100, 0-10, -10-1), and each twin fraction was also racemically twinned with final twin fractions refining to values of 0.14(4), 0.38(5), and 0.25(4). The asymmetric units of $[2]PF_6$ (form b) and $[4]PF_6$ contain two cation/anion pairs. Crystallographic data and refinement details for all of the nine structures solved are presented in Table 1.

Hyper-Rayleigh Scattering. The apparatus and experimental procedures used for the 1300 nm fs HRS studies with high-frequency demodulation of multiphoton fluorescence were

⁽²¹⁾ SAINT (Version 6.45) and SADABS (Version 2.10); Bruker AXS Inc.: Madison, WI, 2003.

⁽²²⁾ Sheldrick, G. M. Acta Crystallogr., Sect. A 1990, 46, 467.

⁽²³⁾ Sheldrick, G. M. SHELXL 97, Program for crystal structure refinement; University of Göttingen; Göttingen, Germany, 1997.

⁽²⁴⁾ SHELXTL (Version 6.10); Bruker AXS Inc.: Madison, WI, 2000.

Table	1. Crystallographic	Data and Refineme	ent Details for Comp	lex Salts [1]PF ₆ , [1]PF6.DMF, [1][PF6	$[0.5[I]_{0.5}, [1]I, [2]PF_0$	6 (forms a and b), [2	2]CI+H2O, [4]PF ₆ , a	nd [5]PF ₆
	$[1]PF_6$	$[1] PF_6 \cdot DMF$	$[1][PF_{6}]_{0.5}[I]_{0.5}$	1[1]	[2]PF ₆ (form <i>a</i>)	$[2]\mathbf{PF}_6$ (form b)	$[2]CI \cdot H_2O$	$[4]PF_6$	$[5]{\rm PF}_6$
formula	C ₂₄ H ₂₂ F ₆ FeNP	C ₂₇ H ₂₉ F ₆ FeN ₂ OP	$C_{48}H_{44}F_6Fe_2IN_2P$	C ₂₄ H ₂₂ FeIN	$C_{29}H_{24}F_6FeNP$	C ₂₉ H ₂₄ F ₆ FeNP	C ₂₉ H ₂₆ ClFeNO	C ₂₆ H ₂₂ F ₆ FeNPS	C ₂₇ H ₂₂ F ₆ FeN ₃ P
M	62.62.6	598.34	1032.42	507.18	587.31	15./.85	495.81	581.33	589.30
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	Cc	Pbca	Cc	$P2_{1/c}$	$\overline{P1}$	$P2_{1/c}$	$P2_{1/c}$	$P2_{1/n}$	$P2_{1/c}$
a/\dot{A}	10.7330(9)	15.7995(9)	12.6010(3)	19.950(3)	9.9910(8)	21.9197(17)	23.543(3)	12.5672(13)	13.7450(15)
b/\dot{A}	24.161(2)	9.7465(6)	36.7520(9)	8.6221(12)	11.7125(10)	10.1163(8)	8.5340(11)	21.354(2)	10.8257(11)
$c/{ m \AA}$	17.3937(15)	34.893(2)	20.0070(5)	12.0759(17)	11.8473(10)	22.2724(17)	11.5240(15)	18.1605(19)	17.4622(19)
α/deg	90	90	90	90	92.4200(10)	90	90	90	90
β/deg	91.912(2)	90	108.0070(12)	104.002(2)	101.7670(10)	90.164(2)	96.700(3)	104.181(2)	112.427(2)
$\gamma/{ m deg}$	90	90	90	90	112.7420(10)	90	90	90	90
$U/Å^3$	4508.0(7)	5373.1(5)	8811.6(4)	2015.5(5)	1240.41(18)	4938.8(7)	2299.5(5)	4725.1(8)	2401.8(4)
Z	8	8	8	4	2	8	4	8	4
T/K	100(2)	100(2)	150(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
μ/mm^{-1}	0.802	0.686	1.457	2.288	0.738	0.741	0.795	0.859	0.765
cryst descript	red plate	brown plate	red rod	red plate	red plate	red plate	orange plate	purple block	purple plate
cryst size/mm	0.30 imes 0.20 imes 0.10	0.30 imes 0.20 imes 0.10	0.30 imes 0.15 imes 0.15	$0.60 \times 0.20 \times 0.10$	0.40 imes 0.15 imes 0.05	0.50 imes 0.40 imes 0.05	0.25 imes 0.20 imes 0.01	0.30 imes 0.20 imes 0.10	$0.45 \times 0.30 \times 0.05$
no. of refins	13 001	36421	28 740	15396	9855	25466	19165	37 427	13 524
no. of indep	6363 (0.0574)	4733 (0.0726)	7871 (0.065)	4126 (0.0351)	4990 (0.0183)	10042 (0.0554)	5354 (0.1502)	9673 (0.0444)	4878 (0.0385)
goodness- of-fit on F^2	0.816	1.050	1.092	1.143	1.049	1.024	0.739	1.081	1.037
final R_1 , wR_2 $\Gamma I > 2\sigma(N)^a$	0.0437, 0.0768	0.0721, 0.1686	0.0560, 0.1331	0.0462, 0.1016	0.0369, 0.0848	0.0498, 0.0959	0.0564, 0.0723	0.0625, 0.0953	0.0596, 0.1449
(all data)	0.0784, 0.0844	0.1043, 0.1868	0.0658, 0.1427	0.0418, 0.0991	0.0454, 0.0888	0.0787, 0.1060	0.1633, 0.0908	0.0464, 0.0894	0.0814, 0.1586
^a The structu	res were refined on $F_{\rm o}$	² using all data; the vi	alues of R_1 are given for	or comparison with o	lder refinements base	d on $F_{\rm o}$ with a typical	threshold of $F_{\rm o} > 4\sigma$	$r(F_{\mathrm{o}}).$	

exactly as described previously.²⁵ All measurements were carried out in acetonitrile, and the reference compound was Disperse Red 1 ($\beta_{1300} = 54 \times 10^{-30}$ esu in chloroform). Local field factors at optical frequencies were applied to account for the use of a different solvent. The residual absorption at 650 nm (solution concentrations up to 3×10^{-3} M) required the application of Lambert–Beer correction factors to the non-linear dependence of $I_{2\omega}/I_{\omega}^2$ on concentration.²⁶ The absence of demodulation, i.e., constant values of β versus frequency, showed that no fluorescence contributions to the HRS signals were present at this measurement wavelength. This situation may indicate (i) a lack of fluorescence, (ii) spectral filtering out of fluorescence, or (iii) the fluorescence lifetime is too short for its demodulation to be observed within the bandwidth of the instrument. The reported β values are the averages taken from measurements at different amplitude modulation frequencies.

Stark Spectroscopy. The Stark apparatus, experimental methods, and data collection procedure were as previously reported,²⁷ except that a Xe arc lamp was used as the light source in place of a W filament bulb. The Stark spectrum for each compound was measured at least twice. The data analyses were carried out as previously described,²⁷ by using the zeroth, first, and second derivatives of the absorption spectrum for analysis of the Stark $\Delta\varepsilon(\nu)$ spectrum. The dipole moment change, $\Delta\mu_{12} = \mu_e - \mu_g$, where μ_e and μ_g are the respective excited- and ground-state dipole moments, associated with each of the optical transitions considered in the fit was then calculated from the coefficient of the second-derivative component. Butyronitrile was used as the glassing medium, for which the local field correction f_{int} is estimated as 1.33.²⁷ A two-state analysis of the ICT transitions gives

$$\Delta \mu_{ab}^{2} = \Delta \mu_{12}^{2} + 4 \mu_{12}^{2} \tag{1}$$

where $\Delta \mu_{ab}$ is the dipole moment change between the diabatic states and $\Delta \mu_{12}$ is the observed (adiabatic) dipole moment change. The value of μ_{12} can be determined from the oscillator strength f_{os} of the transition by

$$|\mu_{12}| = [f_{\rm os}/(1.08 \times 10^{-5} E_{\rm max})]^{1/2}$$
(2)

where E_{max} is the energy of the ICT maximum (in wavenumbers) and μ_{12} is in e Å. The latter is converted into Debye units upon multiplying by 4.803. The degree of delocalization, c_b^2 , and electronic coupling matrix element, H_{ab} , for the diabatic states are given by

$$c_{\rm b}{}^2 = \frac{1}{2} \left[1 - \left(\frac{\Delta \mu_{12}{}^2}{\Delta \mu_{12}{}^2 + 4\mu_{12}{}^2} \right)^{1/2} \right]$$
(3)

$$|H_{ab}| = \left| \frac{E_{max}(\mu_{12})}{\Delta \mu_{ab}} \right| \tag{4}$$

(27) (a) Shin, Y.-g. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. J. Phys. Chem. **1996**, 100, 8157. (b) Coe, B. J.; Harris, J. A.; Brunschwig, B. S. J. Phys. Chem. A **2002**, 106, 897. If the first hyperpolarizability tensor β_0 has only nonzero elements along the ICT direction, then this quantity is given by

$$\beta_0 = \frac{3\Delta\mu_{12}(\mu_{12})^2}{(E_{\rm max})^2} \tag{5}$$

A relative error of $\pm 20-30\%$ is estimated for the β_0 values derived from the Stark data and using eq 5, while experimental errors of $\pm 10-15\%$ are estimated for μ_{12} and $\Delta\mu_{12}$, $\pm 40\%$ for $\Delta\mu_{ab}$, $\pm 30\%$ for H_{ab} , and $\pm 50\%$ for c_b^2 when the Stark spectra can be fit with the experimentally observed spectra.

Results and Discussion

Syntheses and Characterization. The iodide salt of complex 1 has been reported previously and subjected to degenerate four-wave mixing, Z-scan, and nonlinear absorption studies,²⁸ but its quadratic NLO properties have not been investigated to our knowledge. The new chromophores 2-6 were synthesized via Knoevenagel-type condensation reactions between 4-ferrocenylbenzaldehyde and the appropriate picolinium, 1,4-dimethylquinolinium, 2,3-dimethylbenzothiazolium, or 9,10-dimethylacridinium cation. The isolated yields range from 30-65%, except for the salt [6] PF_6 , which was obtained in a low yield of 11% after column chromatography on silica gel. The mixed salt [1][PF₆]_{0.5}[I]_{0.5} was produced serendipitously from a crystallization of $[1]PF_6$ (see below), and as yet, we have unfortunately been unable to isolate this compound in bulk quantities for further study. Adding dissolved/solid KI to an acetonitrile solution of [1]PF₆ or adding dissolved/solid NH_4PF_6 to a methanol solution of [1]I appears to precipitate only the fully metathesized salts, according to elemental analyses.

The identities and purities of the products are confirmed by ¹H spectroscopy, +electrospray mass spectrometry, and CHN elemental analyses. As noted previously for related chromophores with amino electron donors, ^{16,18} the ¹H data allow the three pyridinium units to be ranked according to increasing acceptor strength (deshielding ability) as the N-substituent changes in the order Me < Ph < 2-Pym (2-Pym = 2-pyrimidyl). The lowest field pyridyl doublet signal that is attributable to the protons adjacent to the N atom shifts downfield by ca. 1.1 ppm on moving from [1]PF₆ to [**5**]PF₆, while a corresponding shift of ca. 0.3 ppm is observed for the lowest field ethylenic doublet signal.

Electronic Spectroscopy Studies. The UV-visible absorption spectra of compounds $[1-6]PF_6$ have been measured in acetonitrile, and the results are presented in Table 2. Representative spectra are shown in Figures 2 and 3. Each of the salts $[1-5]PF_6$ displays two dominant absorptions. The origin of these bands in related Fc complexes has been the subject of debate, ^{3a,6b,6c,7} but the most recent analyses by Barlow and co-workers^{6h} indicate that both absorptions are attributable to ICT transitions. The more intense band at higher energy apparently arises from intraligand charge transfer (ILCT), while the less intense lower energy band is predominantly due to metal-to-ligand charge transfer (MLCT).^{6h} The additional relatively intense and sharp UV band observed for $[6]PF_6$ is attributable to $\pi \rightarrow \pi^*$

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Table 2. UV–Visible Absorption and Electrochemical Data for Complex Salts [1–6]PF₆ in Acetonitrile

				$E_{1/2} \text{ or } E, \text{V vs Ag-AgCl} \\ (\Delta E_{\text{p}}, \text{mV})^b$			
salt	$\lambda_{\max}, \operatorname{nm}$ $(\varepsilon, 10^3 \operatorname{M}^{-1} \operatorname{cm}^{-1})^a$	$E_{\rm max}$, eV	assignment	$[E_{1/2}]$ Fe ^{III/II}	$E_{\rm pc}{}^c$		
[1]PF ₆	377 (32.1)	3.29	$\pi \rightarrow \pi^*$	0.52(130)	-1.00		
[2]PF ₆	309 (6.6) 396 (35.2) 529 (8.1)	2.44 3.13 2.34	$\begin{array}{c} \mathbf{d} \rightarrow \pi^{*} \\ \pi \rightarrow \pi^{*} \\ \mathbf{d} \rightarrow \pi^{*} \end{array}$	0.53 (100)	-0.80		
[3]PF ₆	328 (7.8) 415 (27.9)	3.78	$\begin{array}{c} \pi \to \pi^* \\ \pi \to \pi^* \end{array}$	0.50(90)	-0.73		
	539 (8.1)	2.30	$d \rightarrow \pi^*$	0.52(00)	0.72		
[4] PF ₆	409 (35.5) 553 (8.9)	3.03 2.24	$\pi \rightarrow \pi^*$ d $\rightarrow \pi^*$	0.53 (90)	-0.72		
[5]PF ₆	421 (34.7) 561 (9.0)	2.95 2.21	$\begin{array}{c} \pi \longrightarrow \pi^* \\ \mathbf{d} \longrightarrow \pi^* \end{array}$	0.53 (90)	-0.58		
[6]PF ₆	778 (1.4) 363 (16.7)	1.59 3.42	$\pi \rightarrow \pi^*$	0.49(70)	-0.43		
	469 (13.1) 585sh ^d (5.4)	2.64 2.12	$\begin{array}{c} \pi \longrightarrow \pi^* \\ \mathrm{d} \longrightarrow \pi^* \end{array}$				

^{*a*} Solutions $10^{-4}-10^{-5}$ M. ^{*b*} Measured in solutions ca. 10^{-3} M in analyte and 0.1 M in [NBuⁿ₄]PF₆ at a 2 mm disk glassy carbon working electrode with a scan rate of 200 mV s⁻¹. Ferrocene internal reference $E_{1/2} = 0.44$ V, $\Delta E_p = 70-100$ mV. ^{*c*} For an irreversible reduction process. ^{*d*} Very rough estimate due to strong overlap with ILCT band.



Figure 2. UV-visible absorption spectra of the complex salts [1]PF₆ (blue), [3]PF₆ (green), and [6]PF₆ (red) in acetonitrile at 293 K.

excitations within the extended conjugated system of the acridinium (acd) moiety; [3]PF₆ also displays a less intense UV band due to the presence of the quinolinium (quin) unit. It is noteworthy that the 2-Pym chromophore in [5]PF₆ also shows a relatively weak NIR band at ca. 780 nm (Figure 3), which is reproducibly present in several different samples, including crystalline material. The origin of this minor absorption is unclear at present, but is clearly worthy of further investigation.

Moving along the *N*-methyl series [1]PF₆, [3]PF₆, and [6]PF₆, a clear pattern of red-shifting is observed for both the ILCT and MLCT bands (Figure 2). For these two absorptions, respective red-shifts of 0.3 and 0.14 eV are evident on moving from [1]PF₆ to [3]PF₆, and the greater sensitivity of the higher energy band to changes at the electron-accepting end of the chromophore is consistent with its assignment as being ILCT in character. In the case of [6]PF₆, the two bands are strongly overlapped, so the quoted λ_{max} and ε values are only approximations. On moving from [1]PF₆ to [3]PF₆, the relative intensity of the ILCT band



Figure 3. UV-visible absorption spectra of the complex salts [2]PF₆ (purple), [4]PF₆ (orange), and [5]PF₆ (turquoise) in acetonitrile at 293 K.

decreases by ca. 15%, while the MLCT absorption becomes ca. 25% more intense. For [6]PF₆, the intensities of both bands are dramatically decreased, by at least 50% for the ILCT absorption when compared with [1]PF₆. This phenomenon is attributable to diminished π -orbital overlap arising from twisting about the ethylene—acd bond. While X-ray crystallography reveals essentially planar solid-state structures for 4-styryl-*N*-methylquinolinium compounds,²⁹ the presence of the acd unit can be expected to lead to steric interactions between the 2-hydrogen atom of the ethylene bridge and the 1,8-hydrogens of the heterocycle. In accord with this suggestion, the only structural study of a relevant chromophore, (*E*)-9-styrylacridine reveals a large dihedral angle of 67.1(1)° between the two aryl ring systems.³⁰ A previous report of purely organic dyes noted large decreases

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Figure 4. Representation of the molecular structure of the ordered complex cation in the salt [1]PF₆ (50% probability ellipsoids).

in ε of ca. 65% on replacing an alkyl-bzt (bzt = benzothiazolium) unit with a Meacd group, accompanied by red-shifts of ca. 0.4 eV.³¹ Other studies have also revealed relatively low ICT band intensities for Meacd chromophores.³²

For the other three compounds, [2]PF₆, [4]PF₆, and [5]PF₆, the ILCT band intensity is constant and the MLCT band gains only a little intensity on moving from [2]PF₆ to [4/5]PF₆ (Figure 3). However, both bands show steady red-shifts moving along this series. On the basis of the absorption energies (excepting the ILCT E_{max} for [4]PF₆), it is possible to rank the six chromophores according to the strength of their electron-accepting unit as follows: Mepyd < Phpyd < Mequin < Mebzt < 2-Pympyd < Meacd (pyd = pyridinium).

Electrochemical Studies. The complex salts $[1-6]PF_6$ have been studied by cyclic voltammetry in acetonitrile, and the results are presented in Table 2. Each compound shows a reversible oxidation process attributable to the removal of electrons from the electron-rich Fc unit, formally corresponding with a Fe^{III/II} couple. The $E_{1/2}$ values of these waves are almost insensitive to the nature of the electronaccepting substituent, indicating a lack of significant electronic coupling between the two ends of the molecules. The irreversible reduction processes are ascribed to the addition of electrons to the electron-deficient pyd/quin/bzt/acd units. In general, the E_{pc} value increases as the electron acceptor becomes stronger, according to the ordering deduced from the CT absorption spectra (see above). The new acd moiety (in chromophore 6) thus displays the least cathodic reduction potential, consistent with it being the strongest electron acceptor.

Crystallographic Studies. Single-crystal X-ray structures have been obtained for the complex salts [1]PF₆, [1]PF₆. DMF, [1][PF₆]_{0.5}[I]_{0.5}, [1]I, [2]PF₆ (forms *a* and *b*), [2]Cl·H₂O, [4]PF₆, and [5]PF₆. Representations of selected molecular structures are shown in Figures 4–7, and selected interatomic distances and angles are presented in Table 3. The unexpected and relatively unusual mixed salt [1][PF₆]_{0.5}-[I]_{0.5} was produced serendipitously upon crystallization of a sample of [1]PF₆ from which all of the iodide had clearly not been removed by anion metathesis. The same sample, crystallized by diffusion of diethyl ether vapor into a DMF solution, yielded the solvent-free crystals of [1]PF₆. The latter have a distinct plate-like habit, while the crystals of [1][PF₆]_{0.5}[1][PF₆]_{0.5}[1][PF₆]_{0.5}[1][PF₆]_{0.5}[1][PF₆]_{0.5}]



Figure 5. Representation of one of the two independent complex cations in the salt [2]PF₆ (form *b*) (50% probability ellipsoids).



Figure 6. Representation of one of the two independent complex cations in the salt [4] PF_6 (50% probability ellipsoids).



Figure 7. Representation of the complex cation in the salt $[5]PF_6$ (50% probability ellipsoids).

of the sample. It is quite remarkable that a series of DMF/ diethyl ether crystallization experiments involving mixtures of the salts [1]PF₆ and [1]I in varying proportions produced only crystals of the PF₆⁻ salt, which was predominantly present as its DMF solvate [1]PF₆·DMF. Notably, this latter compound adopts a centrosymmetric structure that is quite different from that of [1]PF₆ (see below). Given that the structure of [1][PF₆]_{0.5}[I]_{0.5} appears especially favorable for bulk NLO effects (see below), it is clearly of interest to develop an approach whereby this compound can be isolated reproducibly and in quantity. Several other examples of mixed PF₆⁻/I⁻ salts of transition metal complexes have been crystallographically characterized.³³

It is interesting to note that the two polymorphs of $[2]PF_6$ were obtained from the same crystallization experiment. The monoclinic form *b* has a much larger unit cell that contains eight as opposed to two independent formula units in the triclinic form *a* (Figure 8). The fact that such salts can so readily adopt alternative crystal-packing arrangements under identical macroscopic conditions shows that the differences in stability between them are small. This is perhaps a surprising observation, considering that the

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Table 3. Selected Bond Distances (A) and Dihedral Angles (deg) for Complex Salts [1]PF ₆ , [1]PF ₆ , DMF, [1][PF ₆] _{0.5} , [2]PF ₆ (forms a
and b), [2]Cl·H ₂ O, [4]PF ₆ , and [5]PF ₆ ^{<i>a</i>}

	[1]PF ₆ ^b	[1]PF ₆ ·DMF		[1][PF ₆]	$_{0.5}[I]_{0.5}^{c}$		[2]PF ₆ (form <i>a</i>)	[2]PF ₆ (form $b)^d$	[2]Cl·H ₂ O	[4]F	${}^{e}\mathrm{F_{6}}^{e}$	[5]PF ₆
C(Fc)-C(Ph)	1.476(8)	1.477(6)	1.46(2)	1.48(2)	1.50(2)	1.48(2)	1.474(3)	1.478(4)	1.470(4)	1.477(5)	1.470(4)	1.473(4)	1.472(5)
$C(Ph) - C(Ph)1^{f}$	1.402(10)	1.388(9)	1.41(3)	1.38(3)	1.40(3)	1.40(3)	1.400(4)	1.398(6)	1.403(6)	1.396(7)	1.404(6)	1.397(6)	1.397(7)
$C(Ph) - C(Ph)2^{g}$	1.353(10)	1.376(11)	1.37(3)	1.39(3)	1.38(3)	1.36(3)	1.379(4)	1.379(6)	1.376(6)	1.382(7)	1.381(6)	1.384(6)	1.381(7)
$C(Ph) - C(Ph)3^{h}$	1.405(10)	1.385(12)	1.40(4)	1.39(4)	1.38(3)	1.41(3)	1.404(4)	1.404(6)	1.400(6)	1.389(7)	1.400(6)	1.400(6)	1.406(7)
C(Ph) - C(Eth)	1.448(7)	1.622(13)	1.46(2)	1.45(2)	1.46(2)	1.46(2)	1.455(3)	1.462(4)	1.457(4)	1.463(5)	1.451(4)	1.455(4)	1.453(5)
C(Eth) - C(Eth)	1.331(7)	1.105(10)	1.30(2)	1.39(2)	1.32(2)	1.31(2)	1.344(3)	1.338(4)	1.336(4)	1.342(5)	1.346(4)	1.346(4)	1.345(5)
C(Eth) - C(pyd/bzt)	1.450(8)	1.690(11)	1.46(3)	1.44(2)	1.50(2)	1.47(2)	1.466(3)	1.447(4)	1.448(4)	1.458(5)	1.440(4)	1.439(4)	1.441(5)
$C(pyd) - C(pyd)1^{i}$	1.396(11)	1.366(13)	1.41(4)	1.40(4)	1.40(4)	1.42(3)	1.407(4)	1.404(6)	1.406(6)	1.405(7)	()		1.411(7)
$C(pyd) - C(pyd)2^{j}$	1.354(11)	1.362(11)	1.36(3)	1.39(3)	1.37(3)	1.37(3)	1.364(4)	1.365(6)	1.359(6)	1.363(7)			1.359(7)
$C(bzt) - N(bzt)^k$											1.334(4)	1.332(4)	, í
N(pyd/bzt) - C(Me/Ar)	1.468(7)	1.482(6)	1.53(2)	1.50(2)	1.47(2)	1.52(2)	1.453(3)	1.454(4)	1.452(4)	1.447(5)	1.475(4)	1.464(4)	1.456(5)
dihedral angle 1 ¹	21.1	15.2	6.6	8.8	7.8	6.2	20.9	21.4	24.4	25.0	14.2	30.8	20.9
dihedral angle 2^m	5.8	4.2	7.5	3.4	1.2	3.1	19.3	34.5	16.3	50.9	47.8	23.8	24.4
dihedral angle 3 ⁿ							39.2	44.0	47.8	41.5			19.2

^{*a*} Eth = ethenyl. ^{*b*} For the ordered cation. ^{*c*} For the four independent cations. ^{*d*} For the two independent cations. ^{*f*} For the two independent cations. ^{*f*} Average C(Fc)–CH distance in phenylene ring. ^{*s*} Average CH–CH distance in phenylene ring. ^{*k*} Average C(C)–CH distance in pyd ring. ^{*j*} Average CH–CH distance in pyd ring. ^{*k*} Distance to methylated N atom. ^{*l*} Between planes of C₅H₄ and attached phenylene ring. ^{*m*} Between planes of phenylene and pyd or bzt rings. ^{*n*} Between planes of pyd and *N*-aryl rings.



Figure 8. Crystal-packing diagrams of $[2]PF_6$: (A) form *a* viewed along the crystallographic *a* axis; (B) form *b* viewed along the crystallographic *b* axis (H atoms removed for clarity). The arrows approximate the directions of a selection of the molecular dipolar axes.

strength of Coulombic interactions might be expected to favor a single structure.

Given their strongly dipolar nature, the complexes under investigation might be expected to show some degree of ground-state polarization. However, although the bond distances for the phenylene and pyridyl rings may appear to indicate partially quinoidal resonance forms (Table 3), the observed differences are generally probably not significant. Furthermore, the ethylenic bridges show normal C-C and C=C distances. The structure of unsubstituted (E)-4-stilbazole³⁴ also shows some variations in the phenyl and pyridyl bond distances that follow a similar pattern to those observed here. In addition, the cyclopentadienyl-to-phenylene bond distances in our structures are essentially invariant, and no distortions of the Fc units are observed that would indicate polarization of these donor groups.³⁵ All of these observations are consistent with the electrochemical studies that indicate no significant ground-state electronic coupling between the Fc and pyd units (see above) and also the ¹H NMR J values of ca. 16 Hz that are characteristic of *E*-ethylenic groups. Inspection of the highly variable dihedral angles (Table 3) indicates that these parameters are influenced largely by crystal packing rather than intramolecular electronic effects.

Although this investigation concerns primarily molecular electronic/optical properties, the identification of materials that adopt favorable, polar structures that may display quadratic NLO behavior is clearly of interest for potential applications. Most of the compounds studied here crystallize centrosymmetrically, leading to complete cancellation of the molecular dipole moments (see for example Figure 8). However, [1]PF₆ and [1][PF₆]_{0.5}[I]_{0.5} adopt the *Cc* space group (Table 1), which is the same as that found for the active form of DAST.³⁶ Crystal-packing diagrams for [1]PF₆ and [1][PF₆]_{0.5}[I]_{0.5} are shown in Figure 9 and 10.

In the case of $[1]PF_6$, although the molecular dipoles cancel each other out to some degree (Figure 9A), there is a significant component along the *a* direction (Figure 9B).

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Figure 9. Crystal-packing diagrams of $[1]PF_6$: (A) viewed along the crystallographic *a* axis; (B) viewed along the crystallographic *c* axis (H atoms removed for clarity). The arrows approximate the directions of the molecular dipolar axes.



Figure 10. Crystal-packing diagram of [1][PF₆]_{0.5}[I]_{0.5}, viewed along the crystallographic *c* axis (H atoms removed for clarity). The arrows approximate the directions of a selection of the molecular dipolar axes.

In this structure, the angles between the dipolar axis and the crystallographic *a* axis are approximately 70.7° and 82.5° for the ordered and disordered cation, respectively. For [1][PF₆]_{0.5}[I]_{0.5}, the situation is more promising and a high degree of dipolar alignment is evident, with the chromophores all pointing generally along the *a* direction (Figure 10), meaning that this material should display significant bulk quadratic NLO behavior. For such effects, Zyss and Oudar have defined the optimal angles between the dipolar axis of a chromophore and the polar crystallographic axis as θ_m .³⁷ For the space group *Cc* (symmetry point group *m*), the θ_m value required for phase-matching of SHG is 35.26°, while the EO effect

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Table 4. HRS,	Visible Absor	otion, Stark Sp	pectroscopic,	and Derived	Data for	[1-6]	PF
						4	

salt	$\beta_{1300},^{a}_{10^{-30}}$ esu	$\lambda_{\max}^{b,b}$,	E_{\max}^{b}, eV	$f_{\rm os}{}^b$	$\overset{\mu_{12},^c}{\mathrm{D}}$	$\Delta \mu_{12},^d$ D	$\begin{array}{c}\Delta\mu_{\mathrm{ab}},^{e}\\\mathrm{D}\end{array}$	r_{12}, f Å	$\overset{r_{\mathrm{ab}},^g}{\mathrm{A}}$	c_b^{2h}	$H_{ab}^{i,i}$ 10 ³ cm ⁻¹	$\beta_0,^j$ 10^{-30} esu	$\sum [\beta_0]^k, 10^{-30} $ esu
[1]PF ₆		381	3.25	0.40	5.7	13.3	17.6	2.8	3.7	0.12	8.5	48	85
		521	2.38	0.08	3.0	19.6	20.5	4.1	4.3	0.03	2.8	37	
[2]PF ₆	56 ± 7	399	3.11	0.56	6.9	13.6	19.3	2.8	4.0	0.15	8.9	77	134
		543	2.28	0.09	3.3	23.4	24.4	4.9	5.1	0.02	2.5	57	
[3]PF ₆	47 ± 12	420	2.95	0.44	6.2	13.8	18.6	2.9	3.9	0.13	8.0	73	157
		555	2.23	0.12	3.8	24.6	25.8	5.1	5.4	0.02	2.7	84	
$[4]PF_6$	121 ± 7	416	2.98	0.58	7.2	11.1	18.2	2.3	3.8	0.20	9.4	71	151
		566	2.19	0.12	3.9	22.8	24.1	4.8	5.0	0.03	2.8	80	
[5]PF ₆	317 ± 10	424	2.92	0.67	7.8	17.6	23.5	3.7	4.9	0.13	7.8	143	288
		580	2.14	0.16	4.4	29.3	30.6	6.1	6.4	0.02	2.5	145	
[6]PF ₆	139 ± 2	478	2.59	0.21	4.6	15.2	17.8	3.2	3.7	0.08	5.4	57	150
		599	2.07	0.08	3.2	32.9	33.6	6.9	7.0	0.01	1.6	93	

^{*a*} Obtained from 1300 nm HRS measurements in acetonitrile solutions at 293 K. ^{*b*} Measured in butyronitrile glasses at 77 K (f_{os} is determined by numerical integration of the digitized spectra). ^{*c*} Calculated from eq 2. ^{*d*} Calculated from $f_{int}\Delta\mu_{12}$ using $f_{int} = 1.33$. ^{*c*} Calculated from eq 1. ^{*f*} Delocalized electron-transfer distance calculated from $\Delta\mu_{12}/e$. ^{*s*} Effective (localized) electron-transfer distance calculated from $\Delta\mu_{ab}/e$. ^{*h*} Calculated from eq 3. ^{*i*} Calculated from eq 5. ^{*k*} Sum of the β_0 values derived for the ILCT and MLCT transitions. The quoted cgs units (esu) can be converted into SI units (C³ m³ J⁻²) by dividing by a factor of 2.693 × 10²⁰.



Figure 11. Stark spectra and calculated fits for the ILCT bands of salts [2]PF₆, [5]PF₆, and [6]PF₆ in external electric fields of 4.59, 3.57, and 3.57×10^7 V m⁻¹, respectively. Top panels: absorption spectra (blue = experimental, green = fit), middle panels: electroabsorption spectra (blue = experimental, green = fit) according to the Liptay equation;^{14a} bottom panels: contributions of the 0th (blue), 1st (green), and 2nd (red) derivatives of the absorption spectra to the calculated fits.

requires $\theta_m = 0$, i.e., a fully parallel dipole alignment. In [1][PF₆]_{0.5}[I]_{0.5}, we estimate θ_m as covering the range ca. 14.7–15.8° for the four independent complex cations in the asymmetric unit. This structure is hence not optimized for SHG, but is better suited for EO behavior. Chiffre et al. have previously reported a completely parallel alignment of the molecular dipoles for a neutral 4-nitrophenyl Fc derivative in the P1 space group.^{6j}

Hyper-Rayleigh Scattering Studies. Complex salts $[1-6]PF_6$ have been studied in acetonitrile by using the HRS technique with a 1300 nm laser,²⁵ and the results are presented in Table 4. Although all of the compounds show significant absorption at the second-harmonic wavelength of 650 nm (Figures 2 and 3), readily available alternative fundamental wavelengths such as 1064 and 800 nm would give even greater absorption of the HRS signal. The derived β values are therefore resonance enhanced, but it is not sensible to calculate values of β_0 because for HRS both the MLCT and ILCT transitions contribute to the NLO response simultaneously. Note that β_0 data can be obtained

from HRS measurements only in cases where a single ICT absorption band is observed. Unfortunately, [1]PF₆ did not produce a sufficiently strong HRS signal at 650 nm to allow a reliable derivation of β .

The β_{1300} values generally increase with the electron acceptor strength inferred by the ILCT/MLCT energies on moving along the series [2–5]PF₆ (see above), but the values for [2]PF₆ and [3]PF₆ are not significantly different. Although [6]PF₆ might be expected to have the largest β response on the basis of its relatively low ICT energies (Table 2), the value determined is about half as large as that for [5]PF₆. This result is probably attributable to the lower intensities observed for both the ILCT and MLCT transitions for [6]PF₆.

Stark Spectroscopic Studies. In order to provide further insights into their molecular electronic properties, especially NLO responses, salts $[1-6]PF_6$ have been studied by electronic Stark effect (electroabsorption) spectroscopy in butyronitrile glasses at 77 K, and the results are presented in Table 4. Representative absorption and Stark spectra including all



Figure 12. Stark spectra and calculated fits for the MLCT bands of salts [2]PF₆, [5]PF₆, and [6]PF₆ in external electric fields of 4.59, 3.57, and 3.57×10^7 V m⁻¹, respectively. Top panels: absorption spectra (blue = experimental, green = fit), middle panels: electroabsorption spectra (blue = experimental, green = fit) according to the Liptay equation;^{14a} bottom panels: contributions of the 0th (blue), 1st (green), and 2nd (red) derivatives of the absorption spectra to the calculated fits.

fits for the ILCT bands of [2]PF₆, [5]PF₆, and [6]PF₆ are presented in Figure 11, and the corresponding spectra for the MLCT bands in Figure 12. The low-intensity NIR absorption observed for $[5]PF_6$ in acetonitrile at 293 K (see above) is also present in butyronitrile at 293 K, although it is only poorly resolved; this effect arises from the red-shifting of the visible MLCT band to $\lambda_{max} = 576$ nm, possibly accompanied by a small blue-shift and/or relative intensity decrease of the NIR band. However, in butyronitrile at 77 K, the latter small band is not discernible (Figure 12), because either it is found within the visible MLCT envelope or its intensity becomes greatly diminished in the low-temperature glass. All of the following discussion thus refers to only the intense, visible MLCT bands. The likely presence of an extra relatively weak band under the main visible absorption did not prevent satisfactory fitting of the Stark signal for $[5]PF_6$. Because both the ILCT and MLCT bands for chromophores 1-6 correspond with transitions between a ground and single excited state, it is reasonable to use the standard two-state model³⁸ to estimate β_0 values from the Stark data. Such an approach has previously been adopted by Barlow et al. when studying neutral Fc complexes, although detailed data were not reported.^{6h}

In all cases, both the ILCT and MLCT bands of $[1-6]PF_6$ show small red shifts on moving from acetonitrile solutions to butyronitrile glasses (Tables 2 and 4); with the exception of [4]PF₆, these shifts are a little larger for the MLCT band, but the energy orderings within the series remain constant. The values of f_{os} , μ_{12} , $\Delta \mu_{12}$, $\Delta \mu_{ab}$, r_{12} , and r_{ab} for the MLCT bands of $[1-6]PF_6$ generally increase with the acceptor strength, but f_{os} and μ_{12} for [4]PF₆ are the same as those for [1]PF₆. This latter observation is consistent with the relatively low ε values determined for [4]PF₆ in acetonitrile solution (Table 2). The parameters c_b^2 and H_{ab} for the MLCT bands are essentially constant throughout the series. The f_{os} , μ_{12} , $\Delta \mu_{12}$, $\Delta \mu_{ab}$, r_{12} , and r_{ab} values for the ILCT transitions show similar but less well-defined trends of increasing with acceptor strength, while c_b^2 and H_{ab} again reveal no clear patterns. The ILCT bands always have smaller $\Delta \mu_{12}$, $\Delta \mu_{ab}$, r_{12} , and r_{ab} values when compared with their companion MLCT bands. These observations are consistent with the assigned characters of the two types of transition, since greater distances are involved in the MLCT excitations, and are reminiscent of comments made by Barlow et al. previously.^{6h} In all cases, the ILCT bands show substantially larger values of f_{os} , μ_{12} , c_b^2 , and H_{ab} when compared with the MLCT bands, reflecting the diminished extent of π -orbital mixing inherent in a MLCT as opposed to an ILCT transition. Again in keeping with its relatively low ε value measured in acetonitrile solution (Table 2), the ILCT band of [6]PF₆ shows considerably smaller values of f_{os} and μ_{12} when compared with the other compounds.

For [1]PF₆ and [2]PF₆, the β_0 values derived for the ILCT bands appear larger than those for their MLCT counterparts, but a reverse pattern is observed for $[3-6]PF_6$, although the difference between the two values is only truly significant for [6]PF₆. The estimated total β_0 response generally increases with the strength of the acceptor group indicated by the ICT energies, although the values determined for [4]PF₆ and [6]PF₆ are essentially identical and lower than might be expected. A substantial (ca. 3-fold) increase in β_0 is observed when moving from 1 to 5, and this is consistent with the results of previous studies involving chromophores that combine these acceptor groups with purely organic^{11b,16} or other transition metal-based donors.³⁹ The observed trend arises primarily from decreases in E_{max} , but increases in μ_{12} and $\Delta \mu_{12}$ also play some part (Table 4). A broad agreement with the HRS results is evident, although the latter data are resonance enhanced, and it is noteworthy that both the HRS and Stark measurements

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agree in showing that the 2-Pympyd complex in [5]PF₆ is the most active NLO chromophore among those studied by a considerable margin. Both techniques also indicate that [4]PF₆ and [6]PF₆ have similar β responses. The decreased intensities of the ICT transitions arising from restricted π -orbital overlap (see above) are responsible for lowering the NLO response of [6]PF₆.

It should be emphasized that it is inappropriate to attempt any direct comparisons between the HRS- and Stark-derived β values for several reasons. First, the effects of resonance have not been taken into account in the HRS data. It might therefore be expected that the β_{1300} values determined should be larger than the corresponding $\sum [\beta_0]$ data, while in fact the opposite is generally the case (Table 4). Apart from the fact that there is a trade-off between the requirement to obtain a sufficiently strong HRS signal at 650 nm and the need to avoid excessive reabsorption of this second harmonic light, it is also important to remember that other two-state descriptions are also available, which would change the Stark-derived β_0 values quoted here by a constant factor of either 0.5 or 2.40 The latter data are therefore arguably more useful as a means to reveal structure-activity relationships involving all contributing ICT transitions without any interference from variable resonance effects and also to allow comparisons with benchmark chromophores (see below), rather than necessarily indicating the absolute magnitudes of β_0 responses. Nevertheless, it is worth noting that previous studies with dipolar Ru^{II} ammine complexes have shown that using the two-state eq 5 with a prefactor of 3 (the so-called "perturbation series convention")⁴⁰ often gives remarkably good quantitative agreement with the β_0 values determined via HRS with a 1064 nm laser.^{27b}

Given the inapplicability of the two-state model to deriving β_0 values for Fc chromphores based on data obtained from HRS or EFISHG measurements, the present report provides a rare opportunity to assess the intrinsic (as opposed to resonance enhanced) NLO responses of such complexes. The challenges inherent in obtaining reliable β_0 data, especially from HRS studies, have been discussed on a number of previous occasions.⁴¹ Unfortunately, the only relevant existing report involving Stark studies on Fc species does not include any mention of β_0 values.^{6h} It is noteworthy that the estimated β_0 responses for $[1-6]PF_6$ are relatively large and certainly sufficient for potential technological applications. Given that DAST is now commercial, some direct, quantitative comparisons with our new chromophores are of interest. By using the same approach as described here, except that only a single ICT band ($\lambda_{max} =$ 480 nm, $\mu_{12} = 9.1 \text{ D}$, $\Delta \mu_{12} = 16.3 \text{ D}$) contributes to the NLO response, we have previously derived a β_0 value of 236 \times 10^{-30} esu for the PF₆⁻ analogue of DAST ([DAS]PF₆).^{11b} The fact that this value is about 3 times the total β_0 determined for [1]PF₆ is consistent with the considerably stronger electron-donating ability of a -NMe2 group when compared with Fc. However, the NLO responses of $[3]PF_6$,

[4]PF₆, and [6]PF₆ are more competitive with that of [DAS]PF₆, and [5]PF₆ even shows a possibly larger total β_0 value. This enhanced NLO response has been achieved by combining the Fc donor with a 2-Pympyd acceptor that is rather more powerful than the Mepyd group in [DAS]PF₆. As well as providing valuable insights into the relative magnitudes of the quadratic NLO responses of Fc chromophores, these observations provide a strong incentive to pursue polar materials incorporating new cations, such as 4 and 5, that may show very large bulk NLO effects.

Conclusion

We have synthesized a series of salts of cationic chromophores with electron-rich Fc groups and quaternary nitrogen (QN) electron acceptors, most of which have not been combined with a Fc donor previously. The complexes display both ILCT and MLCT absorption bands that red-shift as the π -electron-accepting ability of the ON unit increases. These observations are corroborated by ¹H NMR chemical shifts and also by cyclic voltammetry, which shows that while the Fc group is reversibly oxidized at an almost constant potential, the irreversible reduction of the QN center becomes steadily more favorable. The β values determined via HRS measurements in acetonitrile at 650 nm are relatively large and generally increase with the acceptor strength of the QN moiety. Stark spectroscopy at 77 K in butyronitrile glasses allows more detailed probing of the molecular electronic properties, and the derived $\Delta \mu_{12}$ values have been used with Oudar's two-state model to give estimated β_0 responses for both the ILCT and MLCT bands. The latter always have larger $\Delta \mu_{12}$ values, but the relative magnitudes of the associated β_0 responses vary. Summation of the values determined for the ILCT and MLCT bands gives total β_0 responses; these generally increase with the strength of the QN group indicated by the ICT energies, in broad agreement with the HRS results. Both techniques also indicate that the NLO response of the chromophore containing the previously unexploited Meacd group is smaller than might be implied simply by the ICT energies, and this can be attributed to a loss of intensity for both ICT transitions due to diminished π -orbital overlap. The new complexes possess β_0 values of similar magnitude or even larger than that of the chromophore in the technologically important material DAST, and the presence of the Fc group also imparts possibilities for switching of NLO responses at the molecular level. Two of the single-crystal X-ray structures determined adopt non-centrosymmetric packing arrangements, with dipole alignment highly favorable for bulk quadratic NLO behavior in one case.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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