

Chemical Communications

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Multielectron C–H Photoactivation with an Sb(V) Oxo Corrole

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Pnictogen complexes are ideal for mediating multi-electron chemical reactions in two-electron steps. We report a Sb(V) bis-μ-oxo corrole that photochemically oxidises the C–H bonds of organic substrates. In the case of toluene, the substrate is oxidised to benzaldehyde, a rare example of a four-electron photoreaction.

Nature utilizes the cytochrome P450 family of enzymes to perform a variety of aerobic oxidations including hydrocarbon hydroxylation, alkene epoxidation, and *N*- and *S*-oxidation.¹ Antimony porphyrins have garnered interest as cytochrome P450 mimics,^{2–4} owing to similarities between the absorption⁵ and magnetic circular dichroism⁶ spectra of Sb(III) porphyrins and the CO adduct of cytochrome P450. Augmenting these spectroscopic relationships, antimony porphyrins mediate a variety of photochemical oxidations^{7,8} including alkene epoxidation^{9,10} and hydrocarbon hydroxylation.^{11,12} These reactions demonstrate that main group complexes can serve as alternatives to transition metal catalysts.^{13–15}

Though less explored,¹⁶ a photo-oxidation chemistry of Sb corroles is presaged by the similarity to the electronic and redox properties of Sb porphyrins. Enhanced spin-orbit coupling from the Sb centre provides ready access to triplet states.¹⁶ These compounds are efficient singlet oxygen (¹O₂) photosensitizers,^{17,18} which can be used for the photoinactivation of mould spores¹⁹ and green algae.²⁰ Other reactions that are prototypical of ¹O₂ include thioanisole oxidation to the sulfoxide and allylic C–H activation to form the hydroperoxide.¹⁷ Additionally, Sb porphyrins²¹ and corroles²² have been utilized as photosensitizers for bromide oxidation, which occurs via an outer-sphere electron transfer process that is coupled to the two-electron reduction of O₂ to H₂O₂.

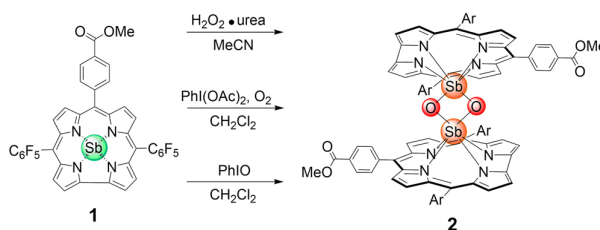


Figure 1. Synthesis of the Sb(V) oxo dimer **2** (Ar = C₆F₅), which can be prepared using various oxidants: H₂O₂ + urea (74% yield), PhI(OAc)₂/O₂ (56% yield), or PhIO (71% yield).

As an alternative to manipulating the Sb–X bond by outer-sphere electron transfer, we have developed a direct halogen multielectron photochemistry by exploiting the Sb(III)/Sb(V)X₂ couple.²³ This approach complements M–X photoactivation at the Mⁿ⁺²X₂ centre of two-electron mixed-valence (Mⁿ...Mⁿ⁺²) complexes with second- and third-row transition metals.^{24–27} Another manifestation of two-electron mixed valency is μ-oxo dimers of first row transition metals bearing macrocyclic ligands.²⁸ Upon irradiation, the Mⁿ–O–Mⁿ moiety is cleaved to generate a Mⁿ⁺¹=O/M^{n–1} pair; the transient Mⁿ⁺¹=O performs oxygen atom transfer (OAT) to the substrate. This two-electron reactivity has been observed for iron,^{29–32} manganese,³³ and ruthenium³⁴ porphyrins, as well as iron corroles^{35,36} and iron phthalocyanines.³⁷ The analogy between two-electron mixed valence chemistry and pnictogen III/V chemistry suggests that four-electron photochemistry may be achieved with Sb(V) dimers. Here, we present the synthesis and characterization of an Sb(V) bis-μ-oxo corrole dimer and demonstrate that this complex undergoes four-electron photochemistry.

The oxidation of the Sb(III) complex **1** to the Sb(V) derivative was accomplished using three different oxidants (Figure 1). The ¹H NMR spectrum of the oxidised product is indicative of a low-symmetry complex, displaying four chemically unique 10-aryl protons at room temperature (see SI). This implies that the antimony centre is out-of-plane and the conformation of the complex is locked, as opposed to the fluxional behaviour of **1** at room temperature.²³ This suggests that the oxidised complex is not a terminal oxo, which would display a ¹H NMR spectrum similar to that of **1**. We thus

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Electronic Supplementary Information (ESI) available: synthetic methods, experimental details, additional characterisation data, and results from DFT and TD-DFT calculations. See DOI: 10.1039/x0xx00000x

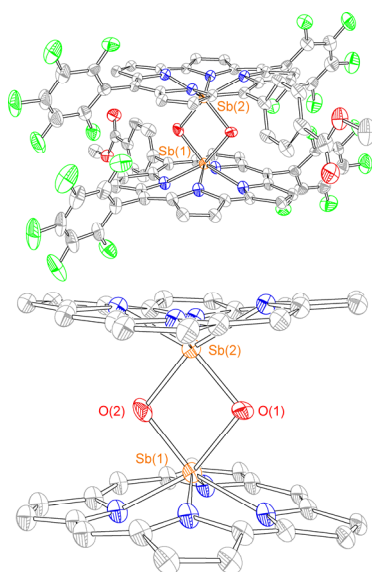


Figure 2. Solid-state crystal structure of **2**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms and solvent molecules have been removed for clarity. The *meso* substituents have been removed from the lower structure to better illustrate the Sb coordination geometry.

suspected that the Sb(V) oxo complex of 5,10,15-tris(pentafluorophenyl)corrole, SbO(TPFC),¹⁷ and other corroles,^{19,38} which were previously formulated as terminal oxo complexes, are indeed bis- μ -oxo corrole dimers. The geometry of **2** was confirmed by X-ray crystallography (Figure 2, Table S1). Bi(III) halide porphyrins exhibit dimeric structures with two bridging halide anions in a diamond core motif,³⁹ akin to **2**, further extending the analogy between bismuth porphyrins and antimony corroles.²³ The distance between the Sb centres is long (~ 3 Å), precluding the formation of a strong Sb...Sb interaction. Similarly, the distance between O atoms is ~ 2.5 Å, which is longer than typical peroxide and superoxide complexes, indicating the absence of a formal O–O bond.

The cyclic voltammogram of **2** (Figure S1a) exhibits two quasi-reversible oxidations at +0.57 V and +0.76 V vs. Fc⁺/Fc, as well as an irreversible reduction at –1.49 V with additional irreversible processes observed outside this window. Similarly, SbO(TPFC) exhibits redox processes at +0.65 V and –1.22 V vs. Fc⁺/Fc.¹⁷ The quasi-reversible waves are attributed to one-electron oxidation of the corrole ligands; this phenomenon is common for cofacial macrocycles that are sufficiently proximate.^{40,41} The CV thus supports the notion that the Sb(V)₂ bis- μ -oxo core is maintained in solution. For the irreversible reduction process, thin-layer spectroelectrochemistry (Figure S1b) reveals the production of **1**.

The electronic absorption spectrum of **2** (Figure 3) exhibits an intense Soret (or B) band in the near-UV and weaker Q bands in the visible. A pronounced emission band is observed at 610 nm (301 cm^{–1} Stokes shift) with a shoulder at 661 nm. The fluorescence quantum yield of **2** is 0.13% with a corresponding lifetime of <80 ps (within the instrument response function, Figure S2). The fluorescence of **2** is weaker than that of water-soluble Sb(V) oxo corroles ($\phi = 2$ –3%).¹⁹ In

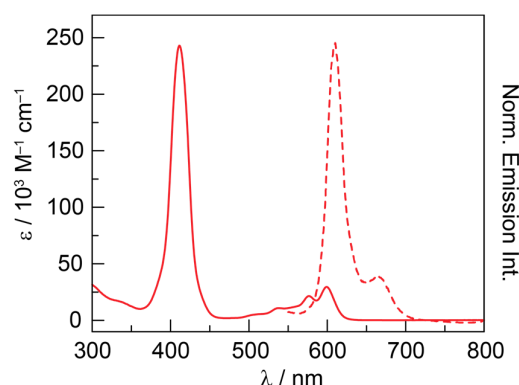


Figure 3. Steady-state absorption (solid lines) and emission (dotted lines) spectra of **2** in toluene ($\lambda_{\text{exc}} = 410$ nm).

the absence of a phosphorescence signature, the triplet state was interrogated using nanosecond transient absorption (TA) spectroscopy (Figure S3). Single wavelength kinetics were monitored at 490 nm and the decay followed biexponential kinetics with characteristic lifetimes of $\tau_1 = 181 \pm 9$ μ s (16%) and $\tau_2 = 15.7 \pm 0.3$ μ s (84%). The shorter component of the fit²³ is due to the photogeneration of **1** (see below). The triplet lifetime of **2** is consistent with that of SbO(TPFC) (160 μ s).¹⁸

The electronic structure of **2** was examined by DFT and TD-DFT calculations. The geometry of **2** was optimized both as a monomer with a terminal oxo and as a dimer with a bis- μ -oxo diamond core (Figures S4–S8, Tables S2 and S3). The calculated geometry of **2** is consistent with the solid-state structure. The dimeric structure of **2** is 1.503 eV lower in energy than two terminal oxo monomers (+35 kcal/mol for Sb₂O₂ (**2**) $\rightarrow$ 2 Sb=O), indicating that there is a significant driving force for dimerization. Since the TD-DFT calculations of **2** as a dimer did not converge due to the large size of the molecule, these calculations were restricted to the monomer subunits (Figure S9, Tables S4 and S5). The calculated UV-vis spectrum qualitatively corresponds to the experimental spectrum. Three states (*S*₅–*S*₇) were calculated in the 350–380 nm region and correspond to the weak UV bands to the blue of the Soret. In each case, the acceptor orbitals are exclusively LUMO+2 and LUMO+3, which have antibonding character with respect to the Sb–O bond (Figures S10 and S11). Similarly, LUMO+4 and LUMO+7 of **2** are antibonding with respect to the Sb–O bond (Figure S11). Therefore, it is expected that irradiation of **2** ($\lambda_{\text{exc}} < 375$ nm) will populate these orbitals and subsequently result in Sb–O bond activation.

The photochemical reactivity of **2** was studied by irradiating a solution of the compound (3–12 μ M) with UV and visible light ($\lambda_{\text{exc}} > 305$ nm) in aerated toluene in the presence of 1,3-cyclohexadiene, a substrate with a weak C–H bond (BDE = 74.3 kcal/mol).⁴² Conversion from **2** to **1** was observed, but isosbestic points were not maintained over the course of the reaction, presumably due to ¹O₂ generation and subsequent decomposition of the corrole. Thus, anaerobic samples were used for all subsequent experiments. Photolysis of **2** in toluene with 1,3-cyclohexadiene maintains isosbestic points for the conversion to **1** (Figure S12a). It should be noted that no conversion to **1** is observed for solutions of **2** stored in the

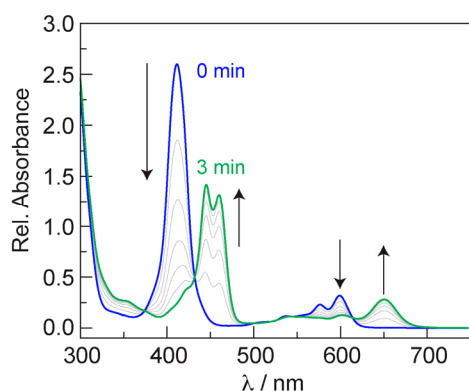


Figure 4. Photolysis ($\lambda_{\text{exc}} > 305$ nm) of an anaerobic sample of **2** in toluene. The initial spectrum of **2** (—) evolves to that of **1** (—) over the course of three minutes. Spectra were recorded every 30 sec.

dark. As a control, **2** was irradiated in the absence of diene. However, the conversion of **2** to **1** was facile ($\lambda_{\text{exc}} > 305$ nm), indicating that toluene ($\text{BDE}(\text{—CH}_3) = 88.5$ kcal/mol)⁴² also serves as a substrate for C–H activation (Figure 4). As a result, benzene ($\text{BDE} = 112.9$ kcal/mol)⁴² was employed as the solvent because it is unreactive under photochemical conditions (Figure S13); conversion of **2** to **1** in benzene with added diene proceeded cleanly (Figure S12b).

A variety of organic substrates, as neat solvents, were evaluated in order to define the limits of **2** to photoactivate C–H bonds. THF ($\text{BDE} = 92.1$ kcal/mol)⁴² is a suitable substrate (Figure S14), but acetonitrile ($\text{BDE} = 96$ kcal/mol)⁴² is not (Figure S15). Additionally, 2-propanol ($\text{BDE} = 91$ kcal/mol)⁴² and cycloheptane ($\text{BDE} = 94$ kcal/mol)⁴² were examined using a 1:1 mixture of the substrate and benzene. For 2-propanol, conversion of **2** to **1** is sluggish (Figure S16) and cycloheptane was unreactive (Figure S17). Given these results, we surmise that **2** is able to activate C–H bonds with $\text{BDE} \leq 92$ kcal/mol under photochemical conditions ($\lambda_{\text{exc}} > 305$ nm).

The photochemical quantum yield for **2** in toluene under monochromatic excitation at 315 nm was $0.18 \pm 0.02\%$. This value is comparable to the quantum yield for toluene activation by a Fe–O–Fe pacman porphyrin ($\phi_{425} = 0.15\%$)³² and higher than that for a Fe–O–Fe corrole dimer ($\phi_{355} = 0.04\%$).³⁵ The kinetics for the photogeneration of **1** were monitored by tracking absorbance changes where **2** does not absorb (Figures S18 and S19). Using neat toluene as the substrate, a significant kinetic isotope effect (KIE) is observed (Figure S20). Analysis of three samples, monitoring both 460 nm and 650 nm, gives $k_{\text{H}} = 1.25 \pm 0.66 \times 10^{-8} \text{ M s}^{-1}$ as compared to $k_{\text{D}} = 6.13 \pm 1.60 \times 10^{-10} \text{ M s}^{-1}$ when the reaction was performed in toluene- d_8 to furnish a $\text{KIE} = k_{\text{H}}/k_{\text{D}} = 20.4$. This value is substantially higher than that for toluene activation by a Fe–O–Fe pacman porphyrin ($\text{KIE} = 1.55$)³² and ethylbenzene activation by a Fe–O–Fe corrole dimer ($\text{KIE} = 3.6$),³⁵ indicating that H-atom abstraction (HAA) is fully rate limiting in the case of **2**. Although this KIE also reflects a solvent isotope effect, the large value (>7) suggests that tunnelling is likely occurring.

The organic products from the photochemical reaction in toluene were identified by GC-MS. Neat toluene (9.38 M) was

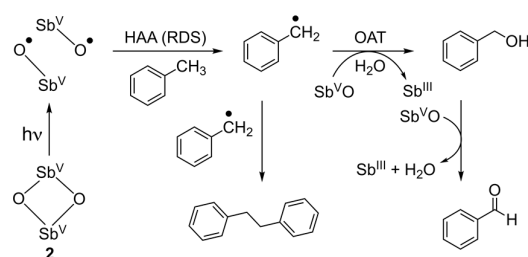


Figure 5. Proposed mechanism for the photochemical oxidation of toluene with **2**.

used containing trace amounts of water ($\sim 0.03\%$ or 16.6 mM, based on the supplier's specifications). The major products were benzaldehyde and benzyl alcohol, observed in a 14:1 ratio (benzaldehyde to benzyl alcohol); trace amounts of dibenzyl were also observed (Figure S21). This result suggests that the four-electron oxidation prevails. An excess (90–100 equiv) of benzaldehyde was detected relative to the amount of **1** formed during photolysis at high photochemical conversion (40–50%). When anhydrous toluene was used, conversion of **2** to **1** was not observed by absorption spectroscopy and no benzaldehyde was detected by GC-MS. This indicates that water is necessary for the reaction to occur and serves as a proton donor. To exclude water as the primary oxygen source for the organic product, a labelling experiment was performed where dry toluene was saturated with ^{18}O water (97 atom %). At low conversion ($\sim 3\%$), only 1.2 equivalents of benzaldehyde were observed per molecule of **1** formed during photolysis. Moreover, the $^{16}\text{O}:^{18}\text{O}$ benzaldehyde product ratio was 9:1, indicating that compound **2** is the primary source of oxygen.

Figure 5 depicts a photochemical reaction sequence that is consistent with the experimental results. The KIE suggests that photon absorption drives HAA from the substrate, shown here to be toluene. The observation of a trace amount of dibenzyl is a consequence of benzyl radical coupling. Formation of the two-electron oxidation product, benzyl alcohol, follows from OAT. A second Sb(V) centre accommodates a second two-electron oxidation to furnish benzaldehyde. Alternatively, the Sb_2O_2 core may directly serve as a four-electron oxidant. Given the prevalence of non-innocent corrole complexes,^{43,44} the reaction could proceed in one-electron steps with the corrole bearing the redox load to avoid the generation of high-energy Sb(IV) intermediates. Based on the ^{18}O experiment, an additional pathway is operative where water serves as the oxygen source. This is also observed under extensive photolysis, where catalytic activity is observed; the amount of product is consistent with the concentration of trace water in the solvent. In this case, the Sb corrole likely serves as a photosensitizer and undergoes a mechanism similar to photochemical oxidations with Sb porphyrins, which utilise water as the O-atom source.^{9–12}

Sb(V)-oxo corroles perform multielectron photoredox chemistry. The X-ray structure of **2** represents the first solid-state structure of an Sb(V)-oxo tetrapyrrole. Calculations show that the absorption bands to the blue of the Soret band of **2** populate orbitals that have antibonding character with respect to the Sb–O fragment. Consistent with these calculations,

steady-state photolysis ($\lambda_{\text{exc}} > 305 \text{ nm}$) of **2** in the presence of a C–H bond with BDE $\leq 92.1 \text{ kcal/mol}$ results in conversion to compound **1** with concomitant C–H activation and OAT. Additional experiments with toluene as the substrate indicate that the reaction has a KIE of 20.4. The primary organic product from the photochemical reaction is benzaldehyde: the four-electron oxidation product. This reactivity is in contrast to transition metal M–O–M complexes with macrocyclic ligands, which undergo two-electron photochemical transformations. Based on labelling studies, the oxygen is primarily derived from compound **2**, although oxygen from water is also incorporated, resulting in apparent catalytic benzaldehyde formation. The ability of Sb(V) centres in the oxo complex to work in concert, in much the same way that metal centres in two-electron mixed-valence complexes do, engenders a rare example of a four-electron phototransformation.

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Supporting Information

Multielectron C–H Photoactivation with an Sb(V) Oxo Corrole

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Materials

The following materials were used as received: hexanes, dichloromethane (CH_2Cl_2), toluene, 1,3-cyclohexadiene, cycloheptane, acetonitrile (MeCN), ethanol (EtOH), benzene, inhibitor-free tetrahydrofuran (THF), 2-propanol, benzonitrile, benzaldehyde, benzyl alcohol, ^{18}O water (97 atom %), urea hydrogen peroxide ($\text{H}_2\text{O}_2\cdot\text{urea}$), iodosobenzene diacetate ($\text{PhI}(\text{OAc})_2$), Nile blue, and silica gel 60 Å 230–400 mesh (40–63 μm particle size) from Sigma-Aldrich; chloroform-*d* (CDCl_3) and toluene-*d*₈ from Cambridge Isotope Laboratories; and iodosobenzene (PhIO) from TCI. Tetrabutylammonium hexafluorophosphate ([TBA][PF₆]) from Sigma-Aldrich was recrystallized from EtOH and subsequently dried under vacuum prior to use. Acetonitrile (MeCN) for electrochemical experiments was obtained from a solvent drying system (Pure Process Technologies) and stored over 3 Å molecular sieves. The Sb(III) complex of 10-(4-methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl)corrole (**1**) was prepared according to literature methods.¹

Synthesis of 10-(4-methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl)corroloto-(oxo) antimony(V) dimer (**2**)

Method 1. In a 50 mL round bottom flask, 16 mg (18 μmol) of the Sb(III) complex of 10-(4-methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl) corrole (**1**)¹ was dissolved in 10 mL of MeCN and 23 mg of $\text{H}_2\text{O}_2\cdot\text{urea}$ (240 μmol) was added. The green solution was sonicated for approximately 1 min to solubilize the urea hydrogen peroxide. The reaction mixture was stirred overnight at room temperature, while protected from ambient light. Over the course of the reaction, the solution turned dark red with a violet hue. Solvent was removed by rotary evaporation, and the residue was collected and then re-dissolved in a minimal amount of CH_2Cl_2 and filtered over a small plug of silica using CH_2Cl_2 as the eluent; the desired product eluted as a red-purple solution. After solvent removal, 12 mg (74% yield) of the title compound was isolated as a red-purple solid.

Method 2. In a scintillation vial, 28 mg of **1** (32 μmol) was dissolved in 5 mL of CH_2Cl_2 and 32 mg of $\text{PhI}(\text{OAc})_2$ (99 μmol) was added. The resultant solution was stirred at room temperature for 1 h. The crude reaction mixture was filtered over a plug of silica gel using CH_2Cl_2 as the eluent. To remove the iodobenzene, the compound was purified on a silica gel column using CH_2Cl_2 as the eluent. The desired product eluted as a red solution, affording 17 mg (56 % yield) of the title compound.

Method 3. In a scintillation vial, 11 mg of **1** (13 μmol) was dissolved in 4 mL of CH_2Cl_2 and 9 mg of PhIO (41 μmol) was added. The resultant solution was stirred at room temperature for 5 min. The crude reaction mixture was filtered over a plug of silica gel, first using hexane to remove the iodobenzene, then CH_2Cl_2 to elute the desired product. Solvent was removed to give 8 mg (71 % yield) of the title compound.

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ 4.20 (s, 6H), 7.55 (d, J = 7.9 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 8.36 (d, J = 4.2 Hz, 4H), 8.38 (d, J = 7.9 Hz, 2H), 8.40 (d, J = 4.7 Hz, 4H), 8.44 (d, J = 7.8 Hz, 2H), 8.51 (d, J = 4.8 Hz, 4H), 8.80 (d, J = 4.2 Hz, 4H). ^{19}F NMR (470 MHz, CDCl_3 , 25 °C) δ -164.63 (m, 4F), -163.11 (m, 4F), -154.11 (t, J = 20.8 Hz, 4F), -139.31 (dd, J^1 = 24.3 Hz, J^2 = 7.4 Hz, 4F), -137.58 (d, J = 22.8 Hz, 4F). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 52.69, 116.89, 121.54, 125.04, 125.62, 126.30, 127.73, 127.84, 128.04, 128.17, 129.18, 131.50, 132.29, 132.75, 134.87, 136.38, 136.86, 139.26, 141.39, 167.18. Anal. Calcd. for $(2\text{M} + \text{H})^+$ and $(\text{M} + \text{H})^+$, $\text{M} = \text{C}_{39}\text{H}_{15}\text{F}_{10}\text{N}_4\text{O}_3\text{Sb}$: 1797.0123 and 899.0101; Found ESI-MS: 1797.0118 and 899.0067. Uv-vis (toluene), λ in nm (ϵ in $10^3 \text{ M}^{-1} \text{ cm}^{-1}$): 411 (242), 510 (5.4), 538 (11), 577 (22), 599 (30). Emission (toluene, λ_{ex} = 410 nm), λ in nm: 610, 661.

Physical Measurements

NMR spectra were recorded on a Varian Inova-500 or JEOL ECZ400S NMR spectrometer at the Harvard University Department of Chemistry and Chemical Biology Laukien-Purcell Instrumentation Centre. ^1H and ^{13}C NMR spectra were internally referenced to the residual solvent signal (δ = 7.26 (^1H) or 77.16 (^{13}C) for CHCl_3 in CDCl_3),² while ^{19}F NMR spectra were externally referenced to α,α,α -trifluorotoluene (δ = -63.72). Mass spectra were recorded on an Agilent 6210 TOF LC/MS mass spectrometer in positive ion mode at the Small Molecule Mass Spectrometry Facility, part of the Harvard FAS Centre for Systems Biology. Gas chromatography-mass spectrometry (GC-MS) analysis was performed using a Shimadzu GC-2010 equipped with a Restek 30 m Rxi-5ms fused silica capillary column interfaced to a Shimadzu QP2010X mass spectrometer via a temperature-programmable transfer line. Helium was used as the carrier gas at a pressure of 150 kPa, giving a linear velocity of 58.9 cm/s. Both the injection port and transfer line were operated at 250 °C. The column was held at 50 °C for 3 min, then increased by 60 °C/min to a final temperature of 250 °C, which was then held for 3.67 min. Calibration curves were generated using authentic samples of benzaldehyde and benzyl alcohol; all samples were spiked with benzonitrile as an internal standard. UV-vis absorption spectra were acquired using a Cary 5000 spectrometer (Agilent) or CCD array spectrophotometer (SI Photonics, Inc). Steady-state emission spectra were recorded on a Photon Technology International (PTI) QM4 fluorometer equipped with a 150 W Xe arc lamp and a Hamamatsu R2658 photomultiplier tube. The relative quantum yield of the Sb corrole in toluene (η = 1.4961)³ was calculated using Nile blue in EtOH (η = 1.3611)³ as the reference (Φ_{ref} = 0.27)⁴ according to the following equation:

$$\Phi_{\text{sam}} = \Phi_{\text{ref}} \left(\frac{\nu_{\text{sam}}}{\nu_{\text{ref}}} \right) \left(\frac{\eta_{\text{sam}}}{\eta_{\text{ref}}} \right)^2 \quad (1)$$

where ∇ is the slope of the plot of integrated fluorescence intensity versus absorbance (constructed with 5 points) and η is the refractive index of the solvent. Air-free corrole samples for transient absorption spectra, triplet lifetimes, and photolysis experiments were prepared using three cycles of freeze-pump-thaw (FPT) to pressures below 10^{-5} Torr. Steady-state photochemical reactions were performed using a 1000 W high-pressure Hg/Xe arc lamp (Oriel). The beam was passed through a water-jacketed filter holder containing a 305 nm long pass filter then through an iris and collimating lens before entering the sample, which was in a quartz cuvette placed in a water-jacketed sample holder to maintain a constant temperature. Electrochemical measurements were made in a glovebox under a nitrogen atmosphere using a CH instruments Electrochemical Workstation using CHI Version 10.03 software. Samples were prepared at concentrations of ~ 1 mM with 0.1 M [TBA][PF₆] as the supporting electrolyte in acetonitrile. Cyclic voltammograms (CVs) were recorded at a scan rate of 100 mV/s using a glassy carbon button working electrode, a Ag wire reference electrode, and a Pt wire counter electrode. The CVs were internally referenced to ferrocene. Thin-layer UV-vis spectroelectrochemistry experiments were performed using a 0.5 mm path length quartz cell with an Ocean Optics USB4000 spectrophotometer and DT-Mini-2GS UV-vis-NIR light source in conjunction with the CH electrochemical workstation described above. Samples were prepared at concentrations of ~ 0.2 mM with 0.1 M [TBA][PF₆] in acetonitrile. Bulk electrolysis was performed using a Pt flag working electrode, a Ag wire reference electrode, and a Pt wire counter electrode.

Femtosecond and Nanosecond Laser Details

Picosecond-resolved emission lifetime measurements were acquired using a Libra-F-HE (Coherent) chirped-pulse amplified Ti:sapphire laser system that has been previously described.⁵ The 800 nm laser output was used to pump an OPerA Solo (Coherent) optical parametric amplifier (OPA); excitation pulses of 400 nm were produced via fourth harmonic generation of the pump beam using a BBO crystal and the pulse power was attenuated to 2–3 mW at the sample using neutral density filters. Emission lifetimes were measured on a Hamamatsu C4334 Streak Scope streak camera, which has been described elsewhere.⁶ The emission signal was collected over a 140 nm window centered at 630 nm with a 1 ns time window using a Stanford Research Systems DG535 delay generator.

Nanosecond transient absorption (TA) spectra were acquired using a previously reported system.^{7,8} Pump light was provided by the third harmonic (355 nm) of a Quanta-Ray Lab-190 Nd:YAG laser (Spectra Physics) operating at 10 Hz. The pump light was passed through a BBO crystal in an optical parametric oscillator (OPO), yielding a visible frequency that was tuned to 600 nm. Excitation light was attenuated to 0.5–2.0 mJ per pulse for all experiments using neutral density filters. Probe white light was generated using a 75 W Xe arc lamp (PTI). The probe beam was aligned with the sample while the laser pump beam was positioned at 15° with respect to the white light probe and both beams were focused

on the sample. After exiting the sample, the light entered a iHR320 monochromator (Horiba Scientific) and was dispersed by a blazed grating (500 nm, 300 grooves/mm) centered at 450 nm. The entrance and exit slits of the monochromator were set to provide a spectral resolution of 2 nm. TA spectra were collected using a gated intensified CCD camera (DH520-25F-01, Andor Technology). Acquisition delays and gate times for the CCD were set using a Stanford Research Systems DG535 delay generator, which was synchronized to the Q-switch output of the laser. The final data were calculated from a combination of four spectra: I (pump on/probe on), I_F (pump on/probe off), I_0 (pump off/probe on), and I_B (pump off/probe off). The resultant TA spectra were obtained using the following equation:

$$\Delta OD = -\log\left(\frac{I-I_F}{I_0-I_B}\right) \quad (2)$$

thereby correcting for both sample emission and extraneous background light. In order to acquire these four spectra, pump and probe beams were selectively exposed to the sample using electronically controlled shutters (Uniblitz T132, Vincent Associates), which were triggered using a Stanford Research Systems DG535 delay generator synchronized to the Q-switch output of the laser. For single wavelength kinetics measurements, output signal from the sample was amplified by a photomultiplier tube (R928, Hamamatsu) and collected on a 1 GHz digital oscilloscope (9384CM, LeCroy); acquisition was triggered using a photodiode to collect scattered laser excitation light.

Computational Details

Density functional theory (DFT) calculations were performed with the hybrid functional Becke 3-parameter exchange functional⁹⁻¹¹ and the Lee–Yang–Parr nonlocal correlation functional (B3LYP)¹² as implemented in the Gaussian 09, Revision D.01 software package.¹³ For light atoms (H, C, N, O, and F), a polarized split-valence triple- ζ basis set that includes p functions on hydrogen atoms and d functions on other atoms (*i.e.* the 6-311G(d,p) or 6-311G** basis set) was used. A Wood-Boring¹⁴ quasi-relativistic effective core potential (*i.e.* MWB46) was used for Sb. All calculations were performed with a polarizable continuum (PCM) solvation model in toluene using a polarizable conductor calculation model (CPCM).^{15,16} All geometries were confirmed as local minima structures by calculating the Hessian matrix and ensuring that no imaginary eigenvalues were present. Excited state calculations were performed using time-dependent DFT (TD-DFT)¹⁷⁻²¹ with the same functionals, basis sets, and solvation details as the ground state, but with the inclusion of diffuse functions on all light atoms (*i.e.* the 6-311++G(d,p) or 6-311++G** basis set). Excited state energies were computed for the 15 lowest singlet and triplet excited states. All optimized geometries and molecular orbitals were rendered in the program Avogadro.²² Simulated UV–vis spectra were generated in the program Gauss View 5 by broadening transition lines with Gaussian functions with a half width of 0.06 eV.

X-ray Crystallographic Details

Diffraction quality crystals were obtained from a toluene solution of the compound at -30°C in a nitrogen atmosphere glovebox, affording crystals of **2** as red plates. X-ray diffraction analysis was performed on a single crystal of **2** coated with Paratone-N oil and mounted on a glass fiber. The crystal was frozen at 100 K by an Oxford Cryosystems cryostream. Radiation was generated from a graphite fine focus sealed tube Mo $K\alpha$ source ($0.71073\text{ \AA}$). Data were collected at the Harvard Department of Chemistry and Chemical Biology X-ray Laboratory on a Bruker D8 diffractometer equipped with a Bruker APEX-II CCD detector. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker AXS SAINT software.²³ Absorption corrections were applied using SADABS.²⁴ The structure was solved using intrinsic phasing using SHELXT^{25,26} and refined using SHELXL^{27,28} operated in the OLEX2²⁹ interface. No significant crystal decay was observed during data collection.

The crystal diffracted very poorly beyond $1.12\text{ \AA}$ resolution, so a resolution of $0.83\text{ \AA}$ could not be achieved. The data used for refinement was integrated to a resolution limit where intensity/sigma > 3 and $R_{\text{int}} < 0.27$. In addition, two strong residual electron density peaks (4.07 and $3.84\text{ electrons/\AA}^3$) were located close to one of the phenyl rings (C65–C70) of the SbO corrole dimer. These peaks are attributed to unresolved twinning that is aggravated by the strong scattering of the Sb centres. The lack of strong reflections precluded the identification and refinement of additional twin domains. The weak diffraction of the crystal and unresolved twinning led to a structure that is of inadequate quality for accurate determination of bond distances and angles. Thus, only the overall connectivity and arrangement of molecules should be interpreted from the structure.

While four toluene solvent molecules were located and modeled in the structure, a small portion of the structure contains electron density that could not be modeled. This electron density likely arises from severely disordered toluene solvent molecules. Consequently, the unassigned electron density was accounted for using SQUEEZE³⁰ as implemented in the PLATON interface. As a result of the low resolution and unresolved twinning, a stable refinement was only achieved by using strong atomic displacement restraints (RIGU, SIMU, and in select cases EADP) on the SbO corrole dimer. Geometric constraints (AFIX) were applied to the phenyl ring (C65–C70) close to the strong residual electron density peaks. Atomic displacement parameter restraints (RIGU and SIMU) as well as geometric constraints (AFIX) were also applied to the toluene solvent molecules in the crystal. One toluene molecule was found to be disordered over two positions. The relative occupancies of each of these positions were refined against each other ($53(2):47(2)$) and then fixed in the final refinement. The disordered toluene molecule required additional distance (DFIX and SADI) and geometric (FLAT) restraints. Hydrogen atoms were placed in ideal positions and refined using the riding model. The structure gives rise to A and B level alerts from

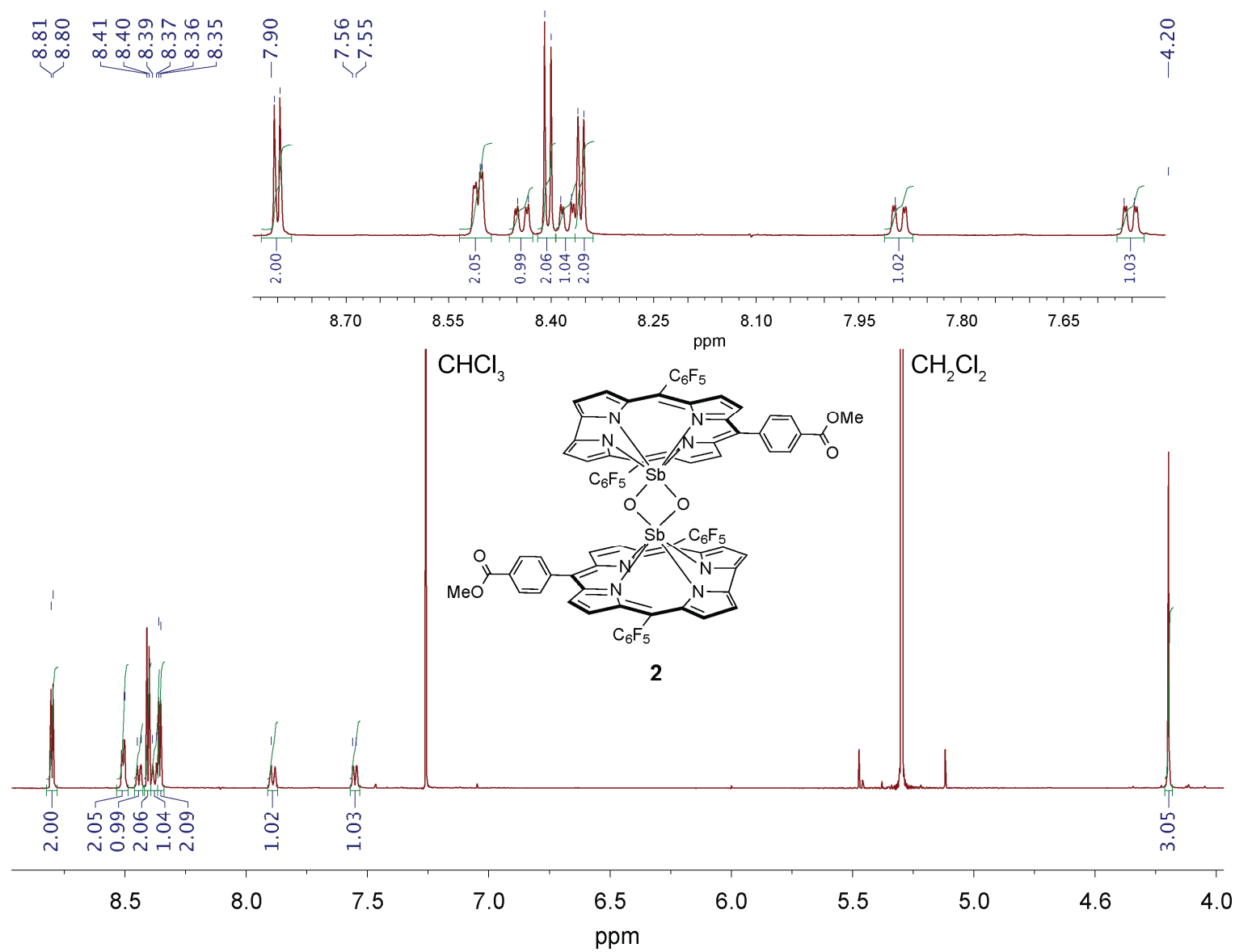
checkCIF. Responses addressing these alerts have been included in the CIF and can be read in reports generated by checkCIF.

Unit cell parameters and solution statistics for the structure are summarised in Table S1. Thermal ellipsoid plots are drawn at the 50% probability level with hydrogen atoms and solvent molecules removed for clarity.

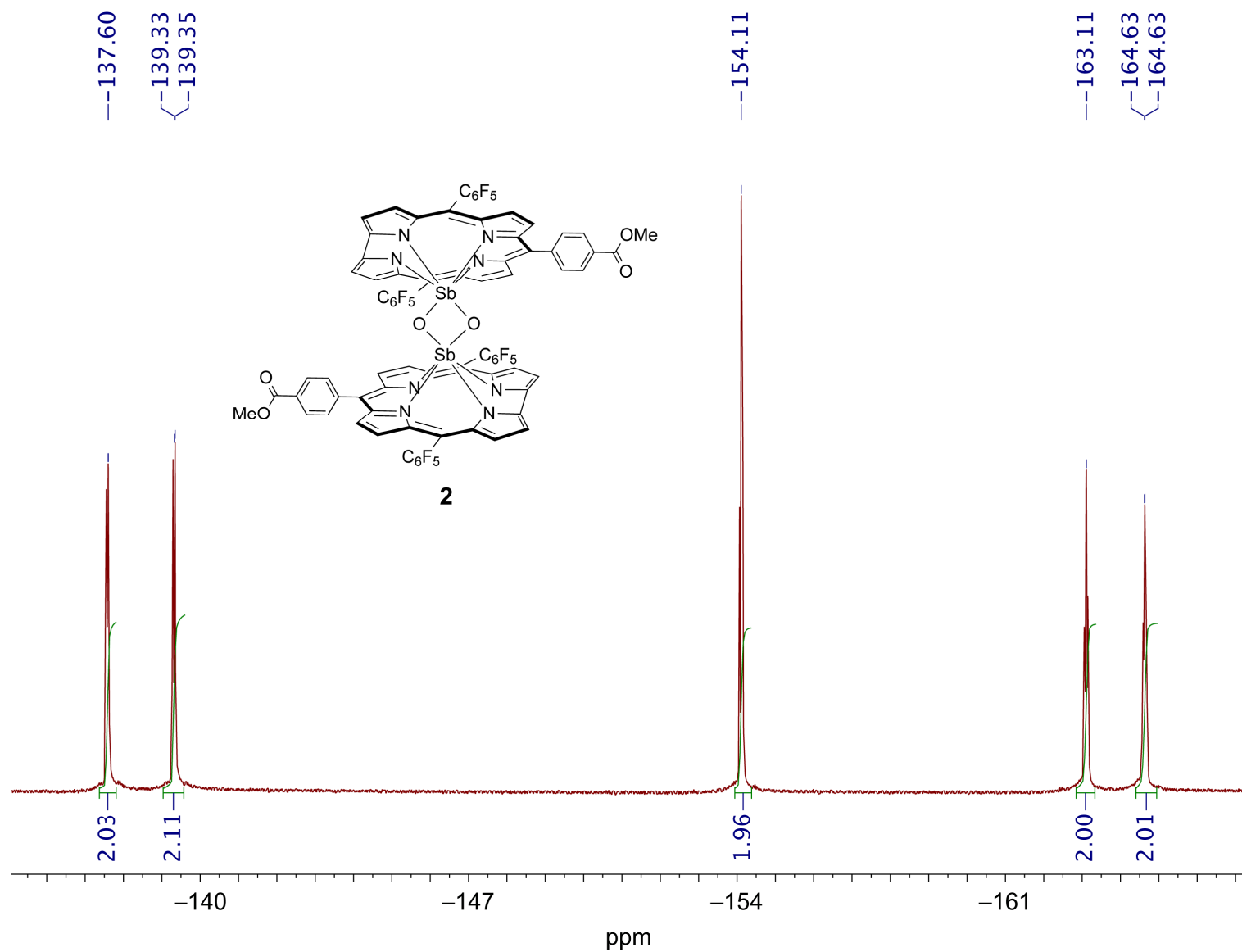
NMR Spectral Details

All NMR spectra were recorded in CDCl₃ at 25 °C at 500 MHz for ¹H spectra, 470 MHz for ¹⁹F spectra, or 100 MHz for ¹³C spectra. The ¹H, ¹⁹F, and ¹³C spectra of **2** are presented on the following pages.

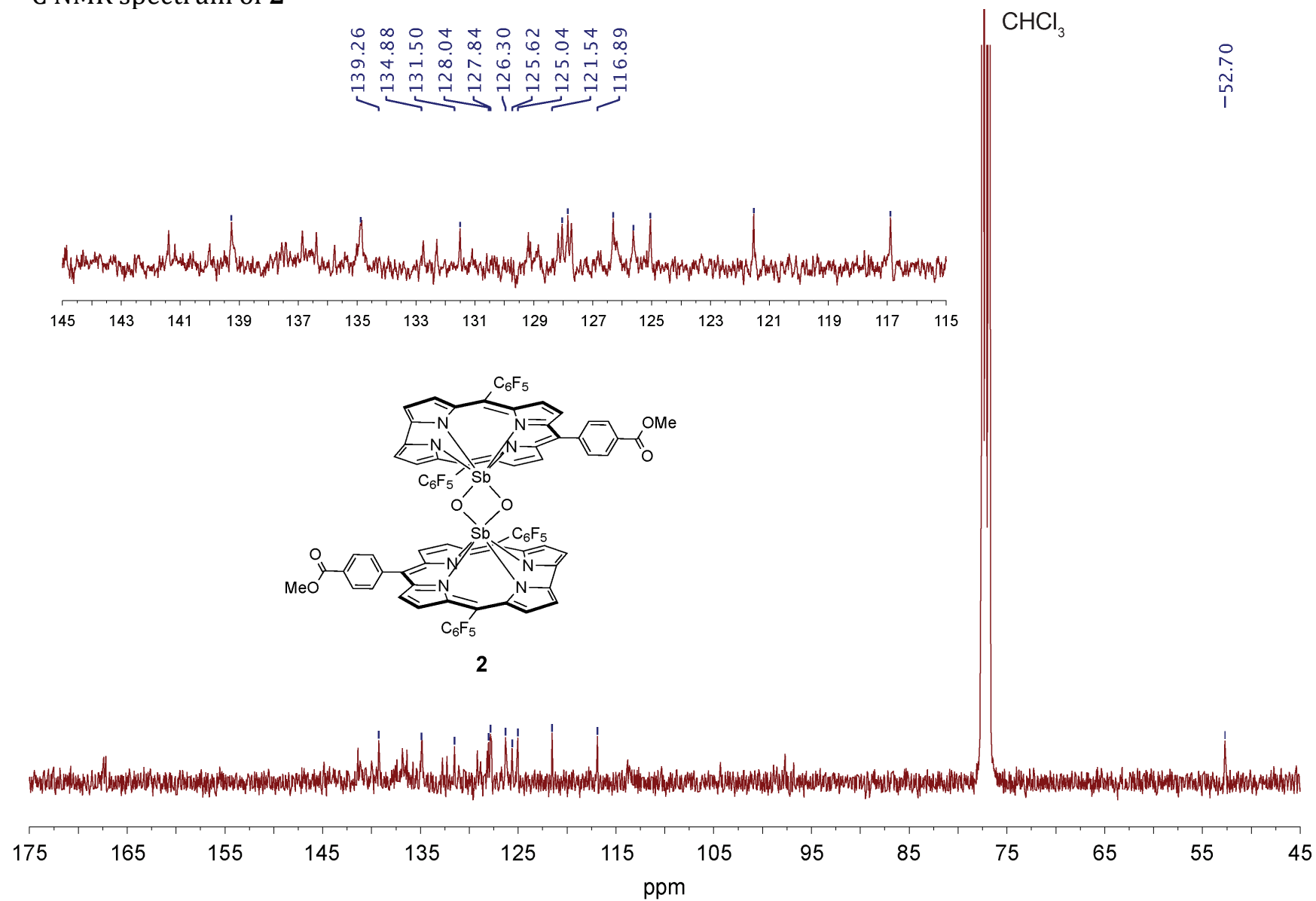
^1H NMR spectrum of **2**



^{19}F NMR spectrum of **2**



¹³C NMR spectrum of **2**



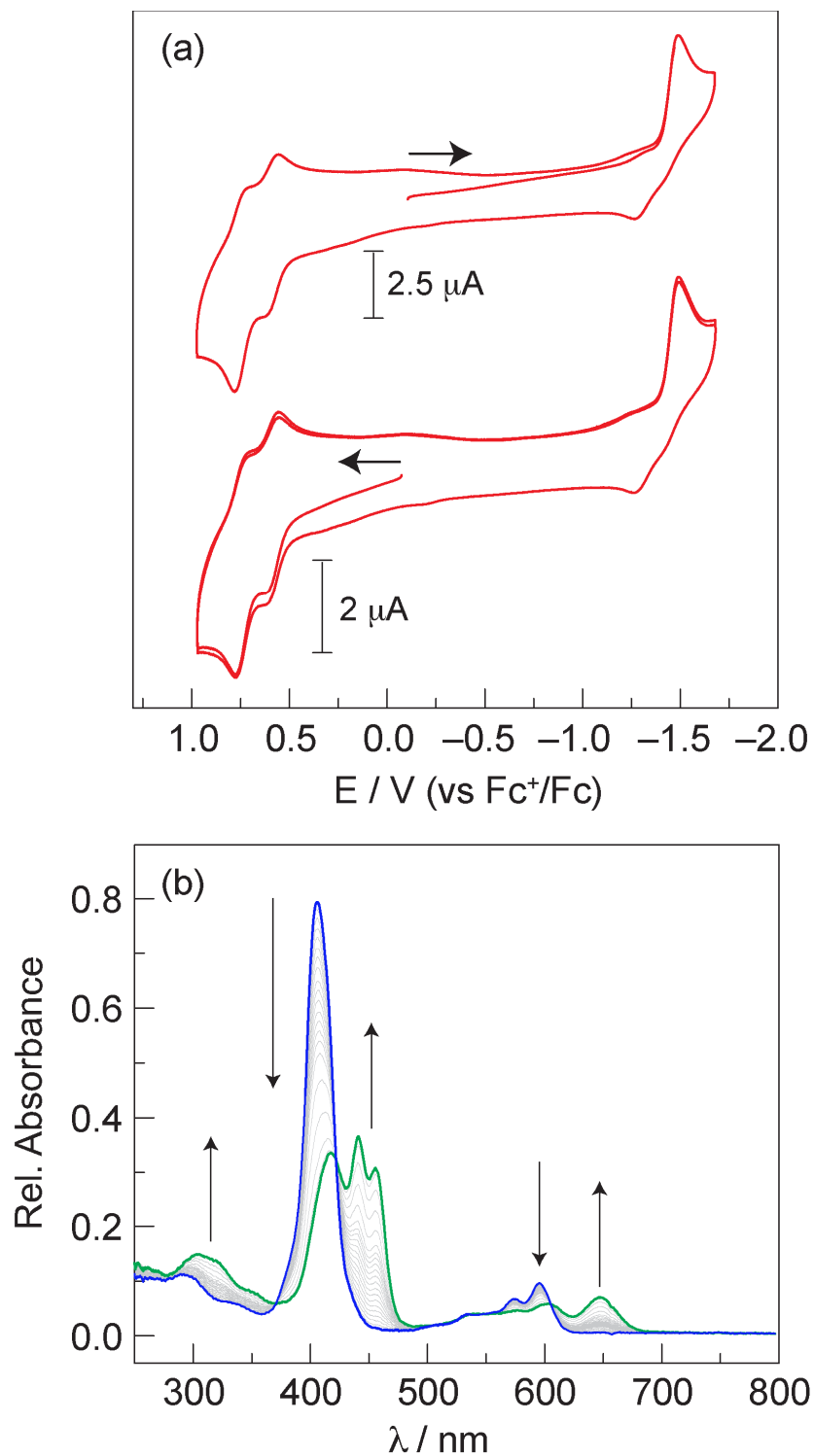


Figure S1. (a) Cyclic voltammogram of **2** in MeCN with 0.1 M [TBA][PF₆] recorded at 100 mV/s under a nitrogen atmosphere. Identical CVs are obtained when the initial scan is run in the cathodic or anodic direction. (b) Spectroelectrochemistry of **2** with bulk electrolysis conducted at -1.8 V vs. Fc⁺/Fc, showing the reduction to **1**.

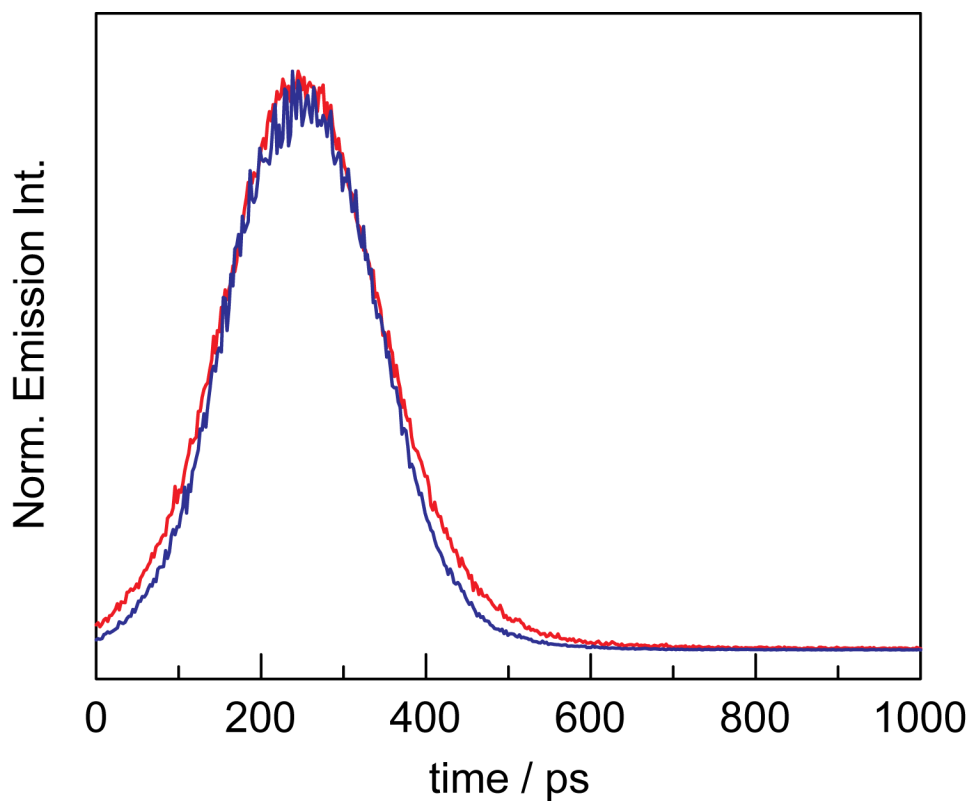


Figure S2. Fluorescence decay trace for **2** (—) in aerated toluene. Since this trace is on the order of the instrument response function (—), it is not possible to extract meaningful lifetimes from this data. As a result, the fluorescence lifetimes are estimated to be < 80 ps. This value represents the return of the signal to baseline (~400 ps), assuming that this process takes five lifetimes.

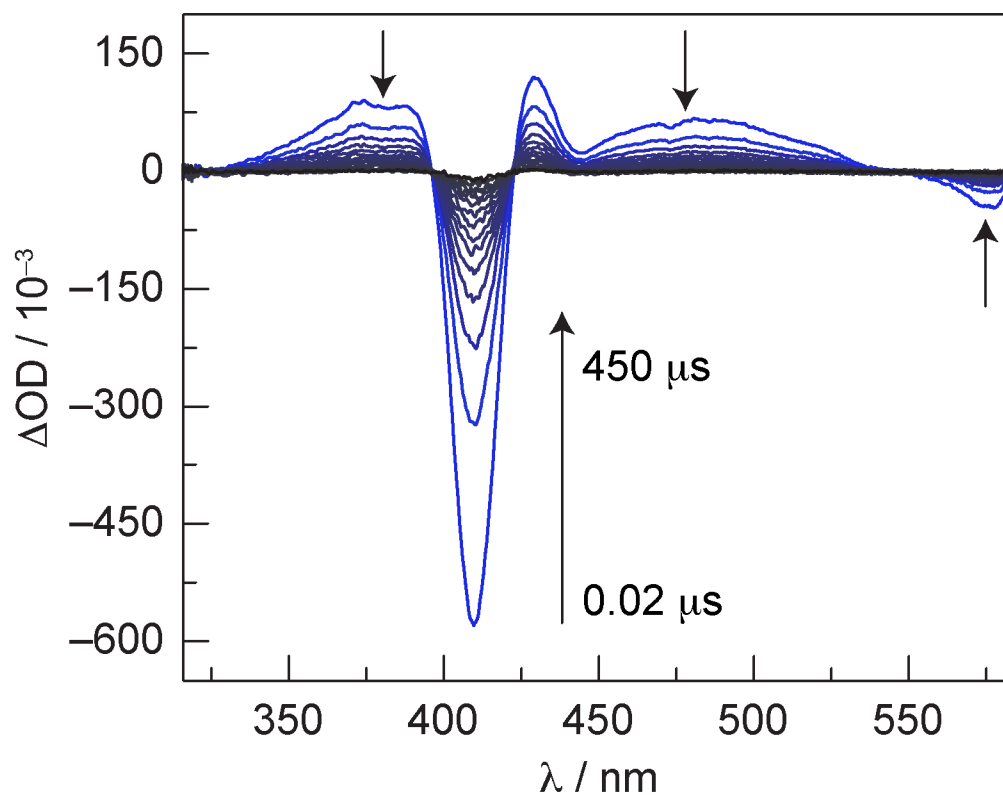


Figure S3. Nanosecond transient absorption (TA) spectra ($\lambda_{\text{exc}} = 600 \text{ nm}$) of a freeze-pump-thawed toluene solution of **2**, showing the bleach of the ground state with concomitant growth of the triplet state. Temporal evolution is from 20 ns (prompt spectrum) to 450 μs in 30 μs intervals.

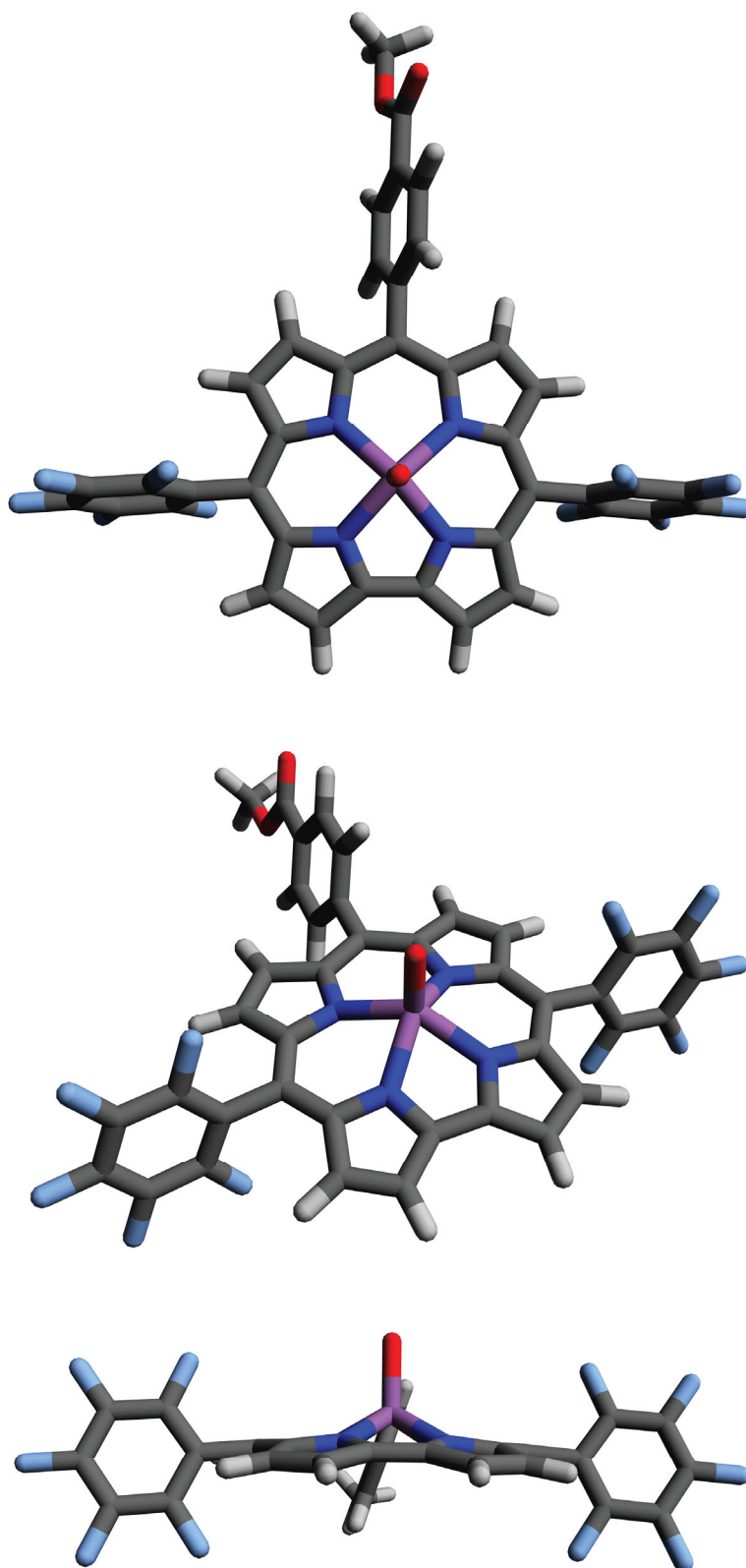


Figure S4. DFT-optimized geometry of **2** monomer using the 6-311G** basis set.

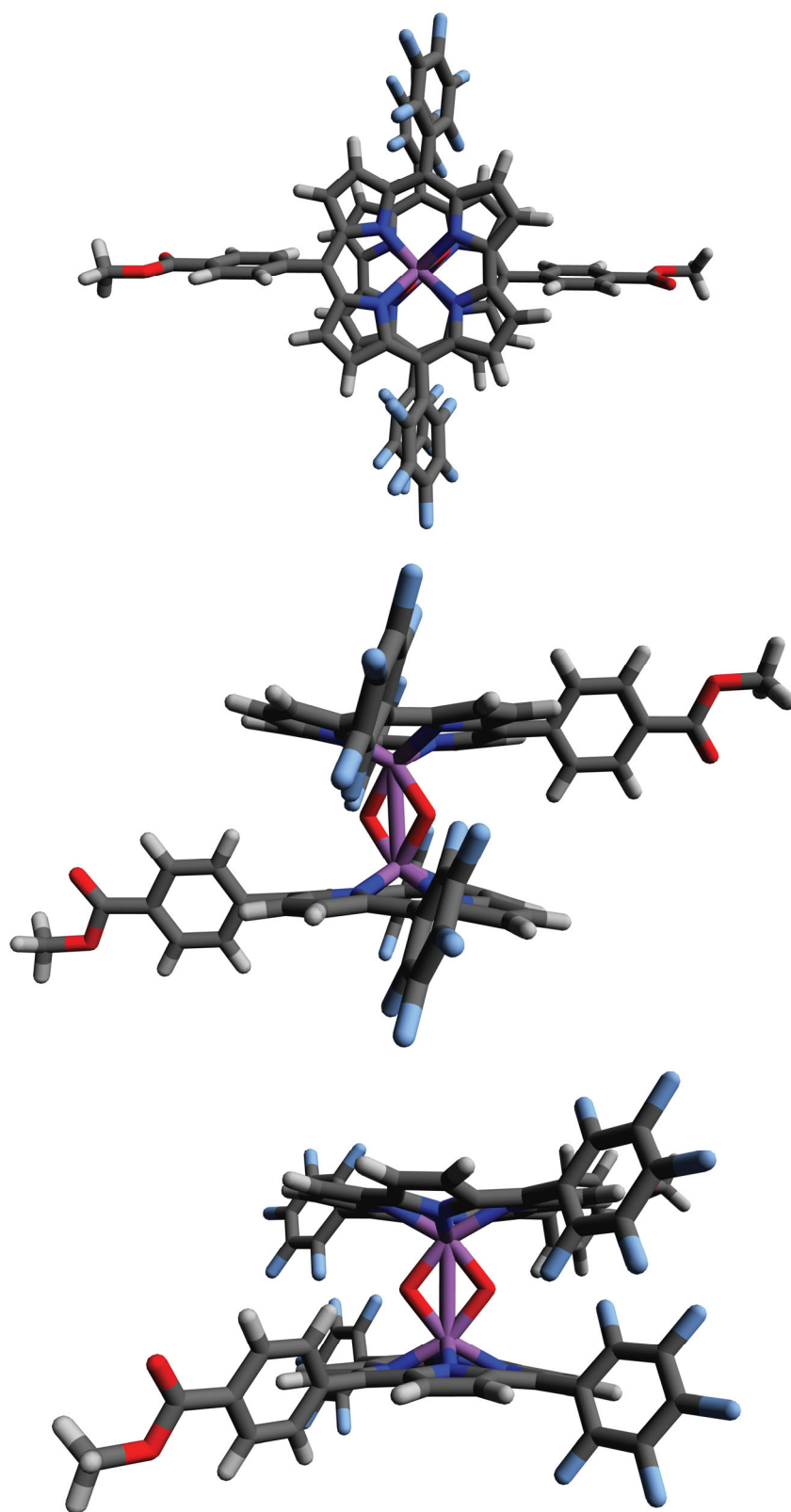


Figure S5. DFT-optimized geometry of **2** using the 6-311G** basis set.

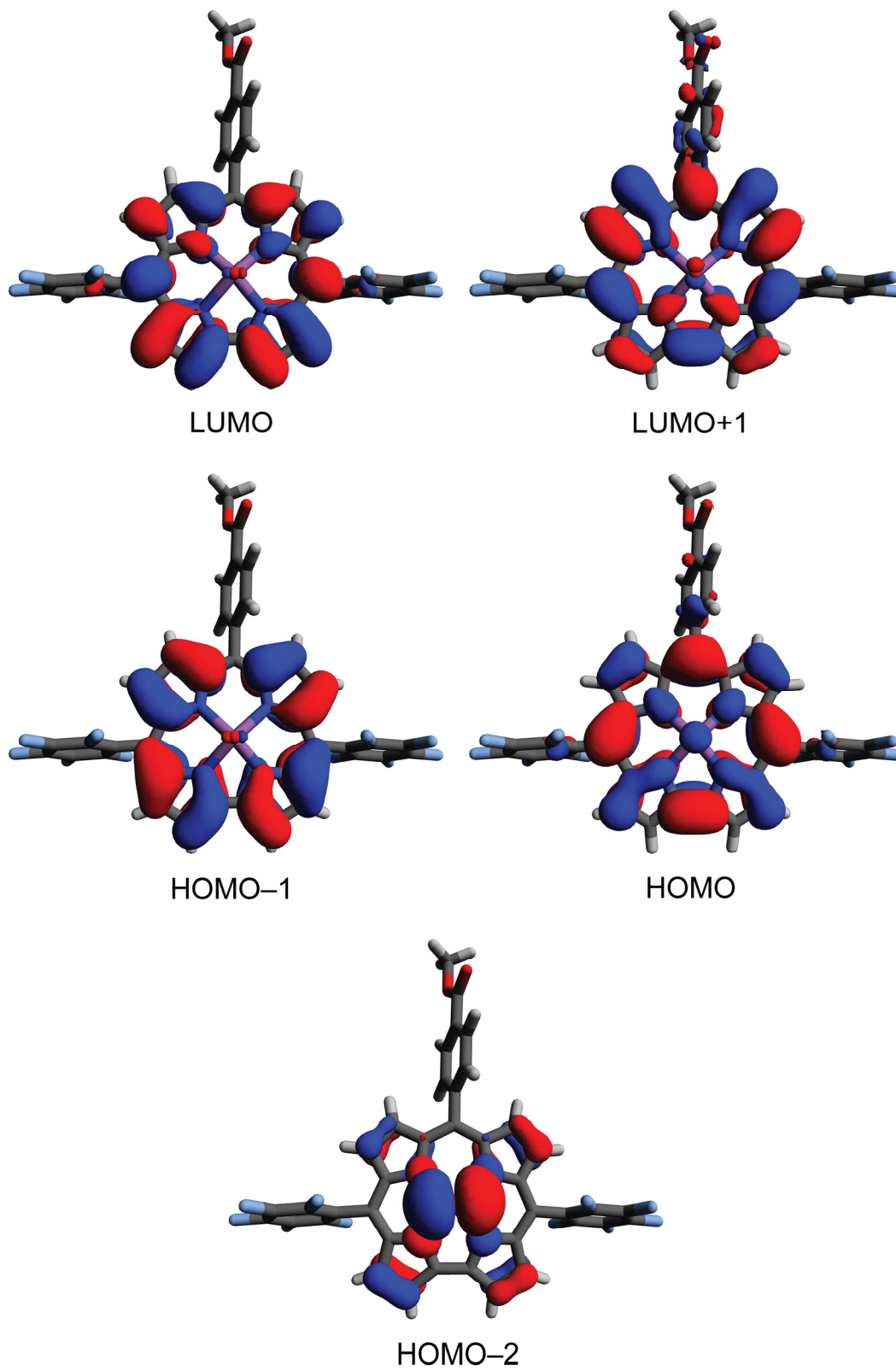
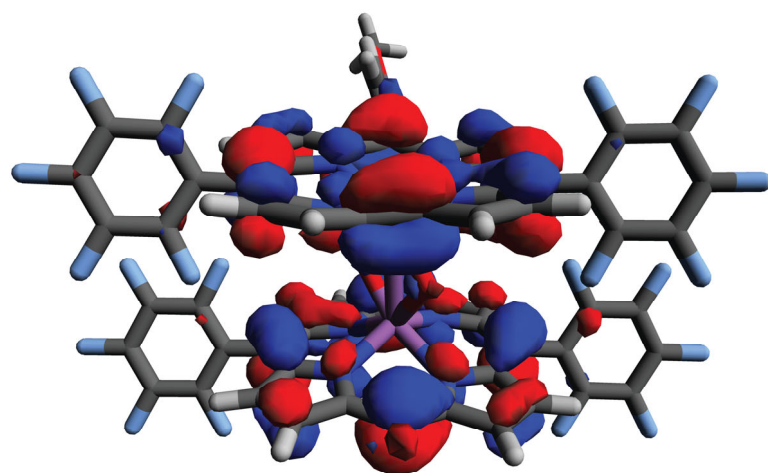
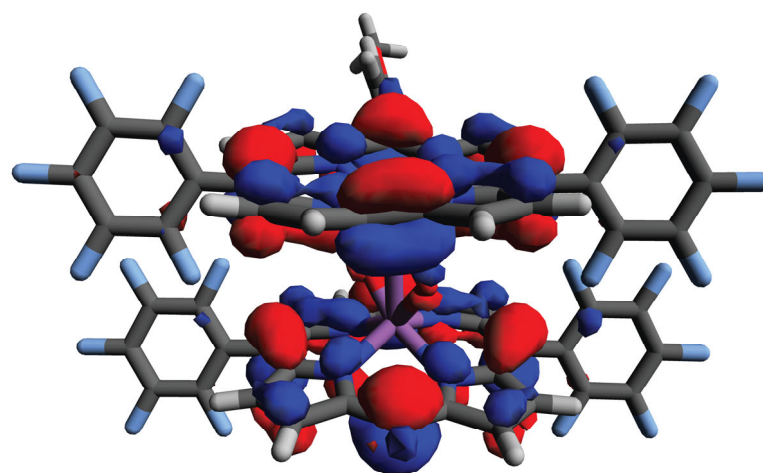


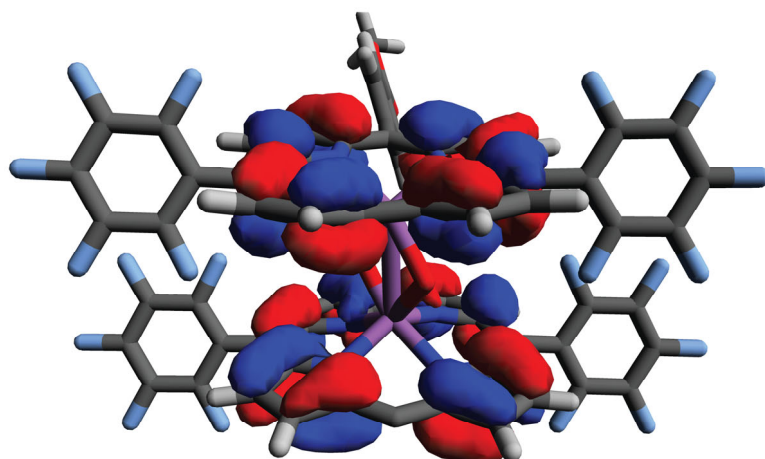
Figure S6. Frontier molecular orbitals of **2** monomer.



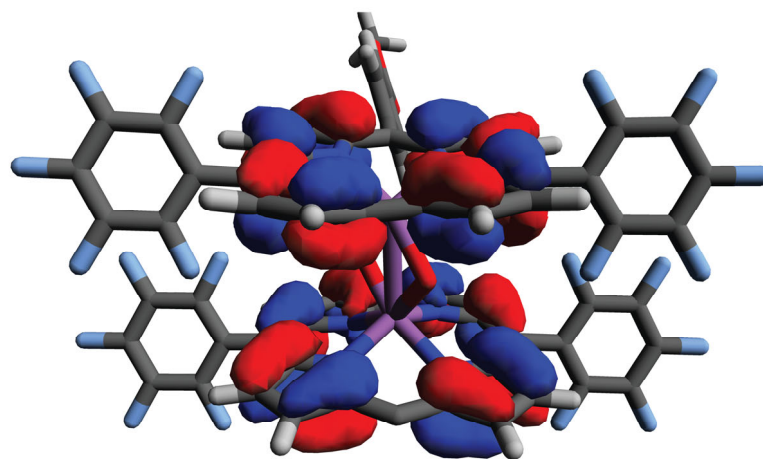
HOMO-1



HOMO



HOMO-3



HOMO-2

Figure S7. The four highest occupied molecular orbitals of **2**. Both HOMO-3 and HOMO-2 of the dimer are comparable to the HOMO-1 of **2** monomer, whereas HOMO-1 and HOMO are similar to the HOMO of **2** monomer. One of the 10-aryl substituents has been removed for clarity.

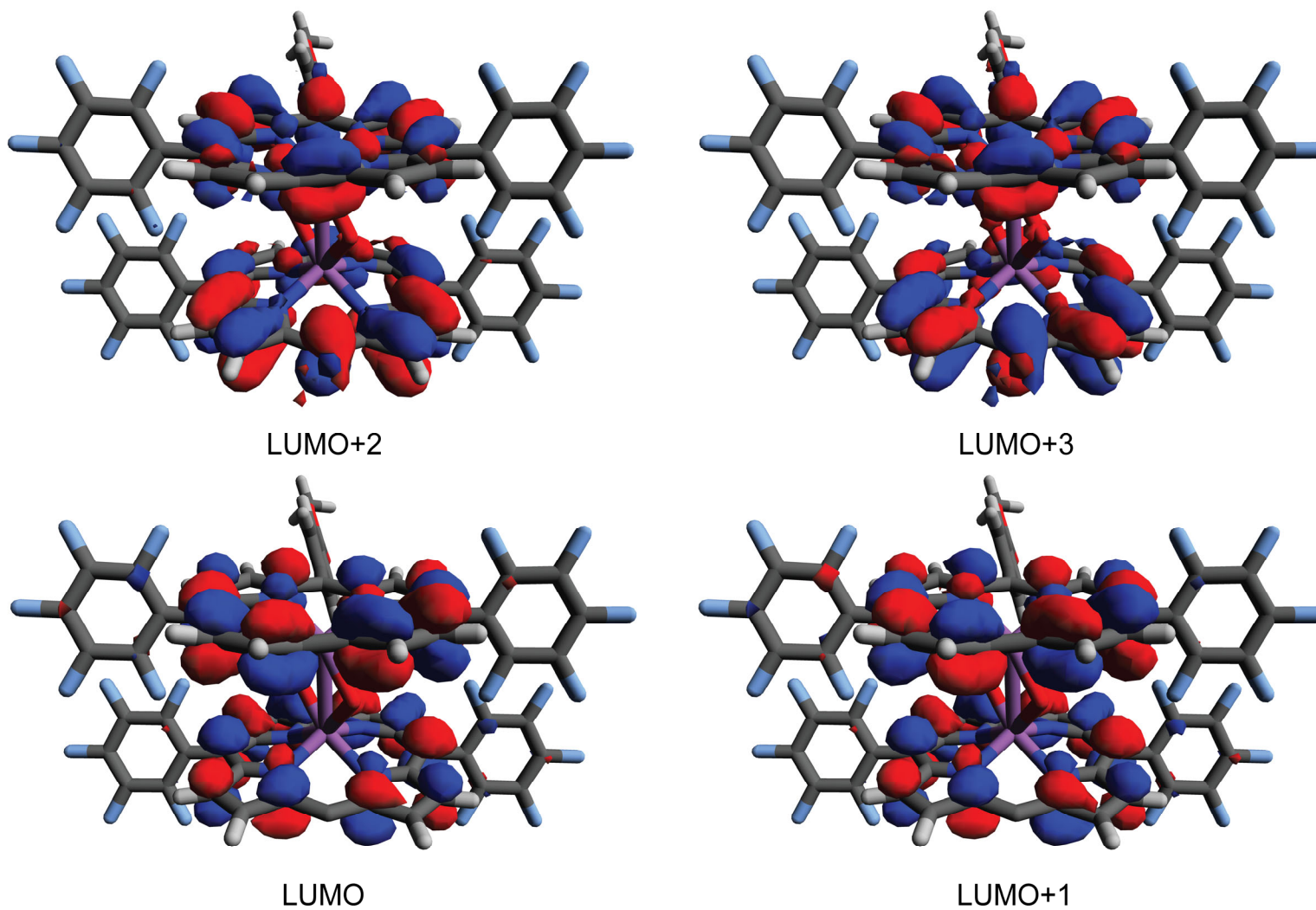


Figure S8. The four lowest unoccupied molecular orbitals of **2**. Both LUMO and LUMO+1 of the dimer are comparable to the LUMO of **2** monomer, whereas LUMO+2 and LUMO+3 are similar to the LUMO+1 of **2** monomer. One of the 10-aryl substituents has been removed for clarity.

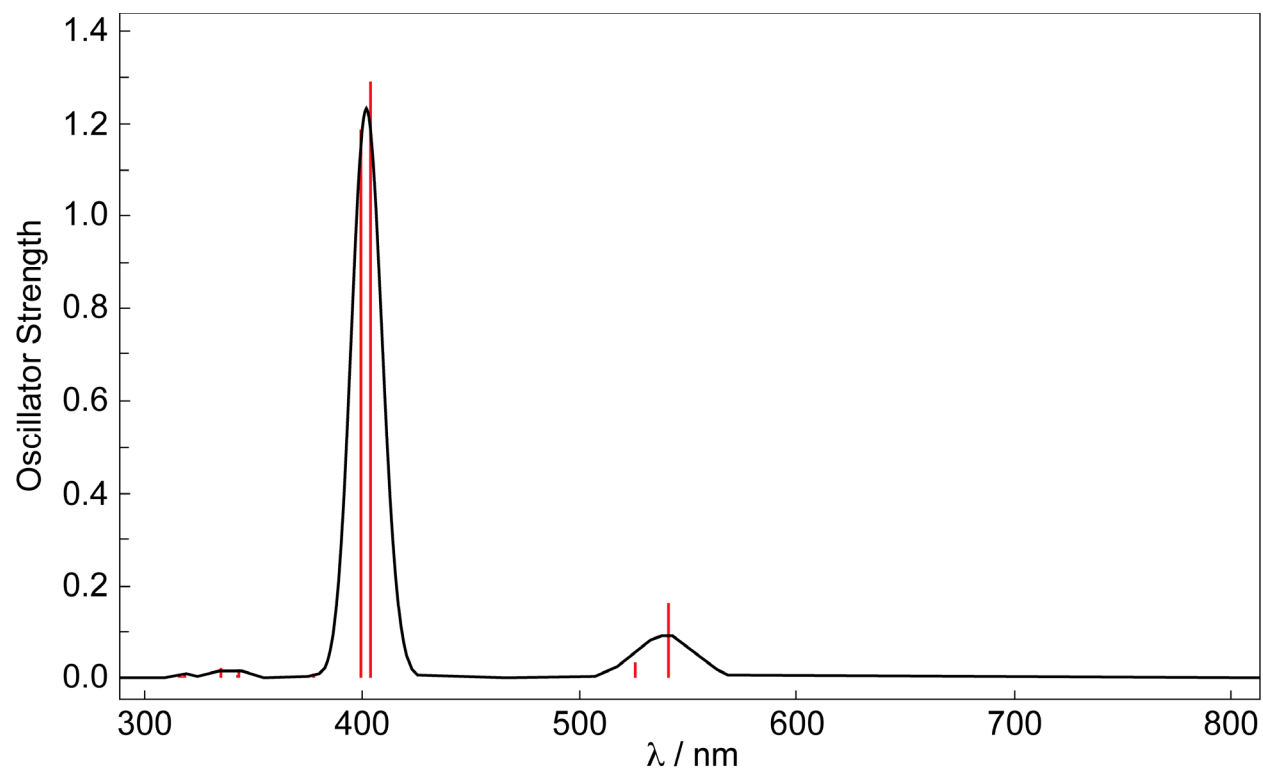


Figure S9. Simulated UV-vis spectrum of **2** monomer. The transition lines have been broadened with Gaussian functions that have a half width of 0.06 eV.

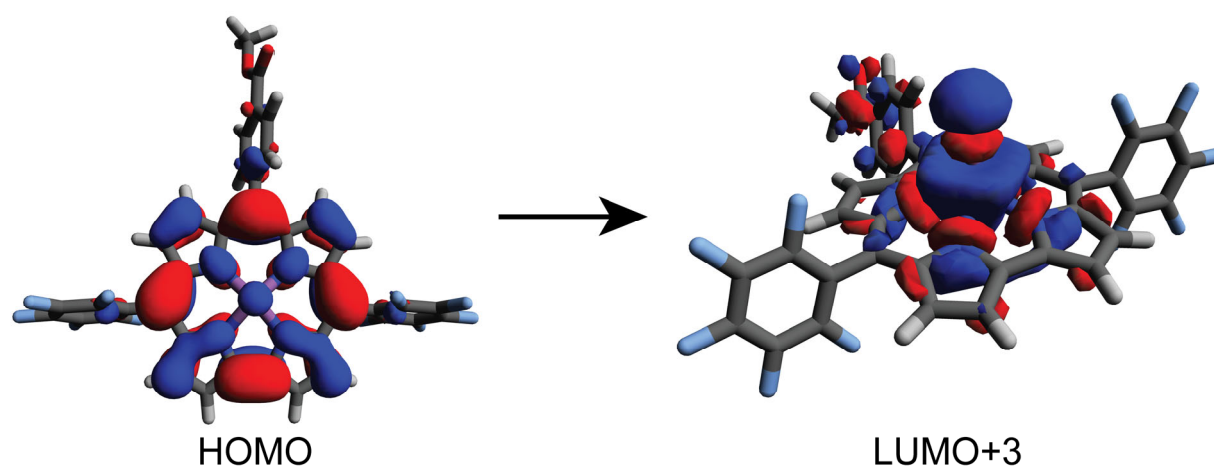
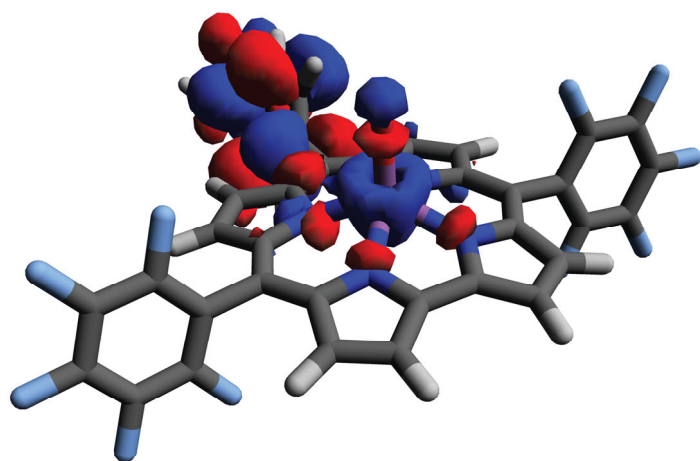
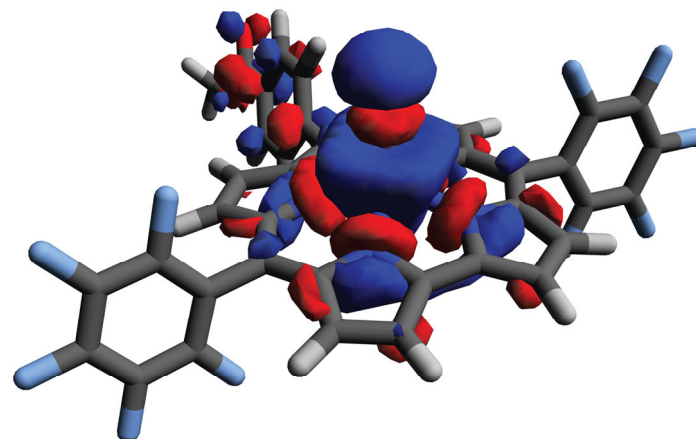


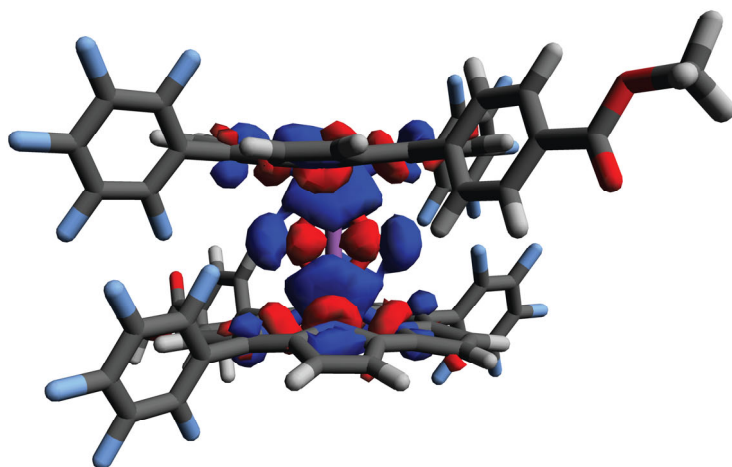
Figure S10. Illustration of the primary (87%) orbital transition associated with S₅ of compound **2** monomer that corresponds to the UV absorption bands to the blue of the Soret band.



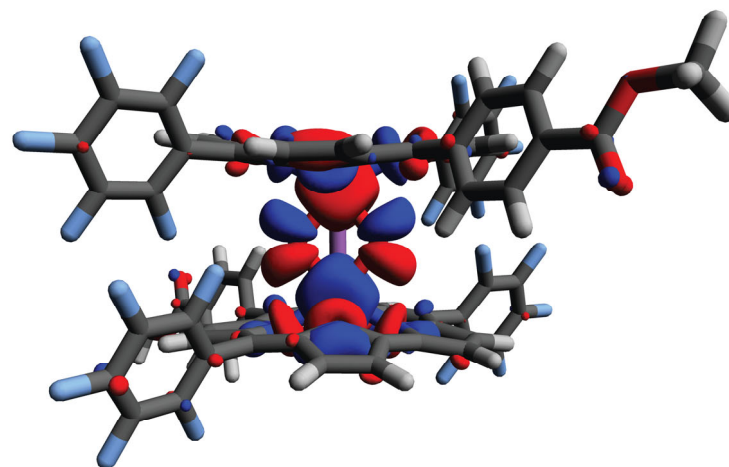
LUMO+2



LUMO+3



LUMO+4



LUMO+7

Figure S11. Unoccupied orbitals of **2** monomer (LUMO+2, LUMO+3) and **2** (LUMO+4, LUMO+7) that exhibit antibonding character with respect to the Sb–O bond. These orbitals are populated in the UV transitions to the blue of the Soret band.

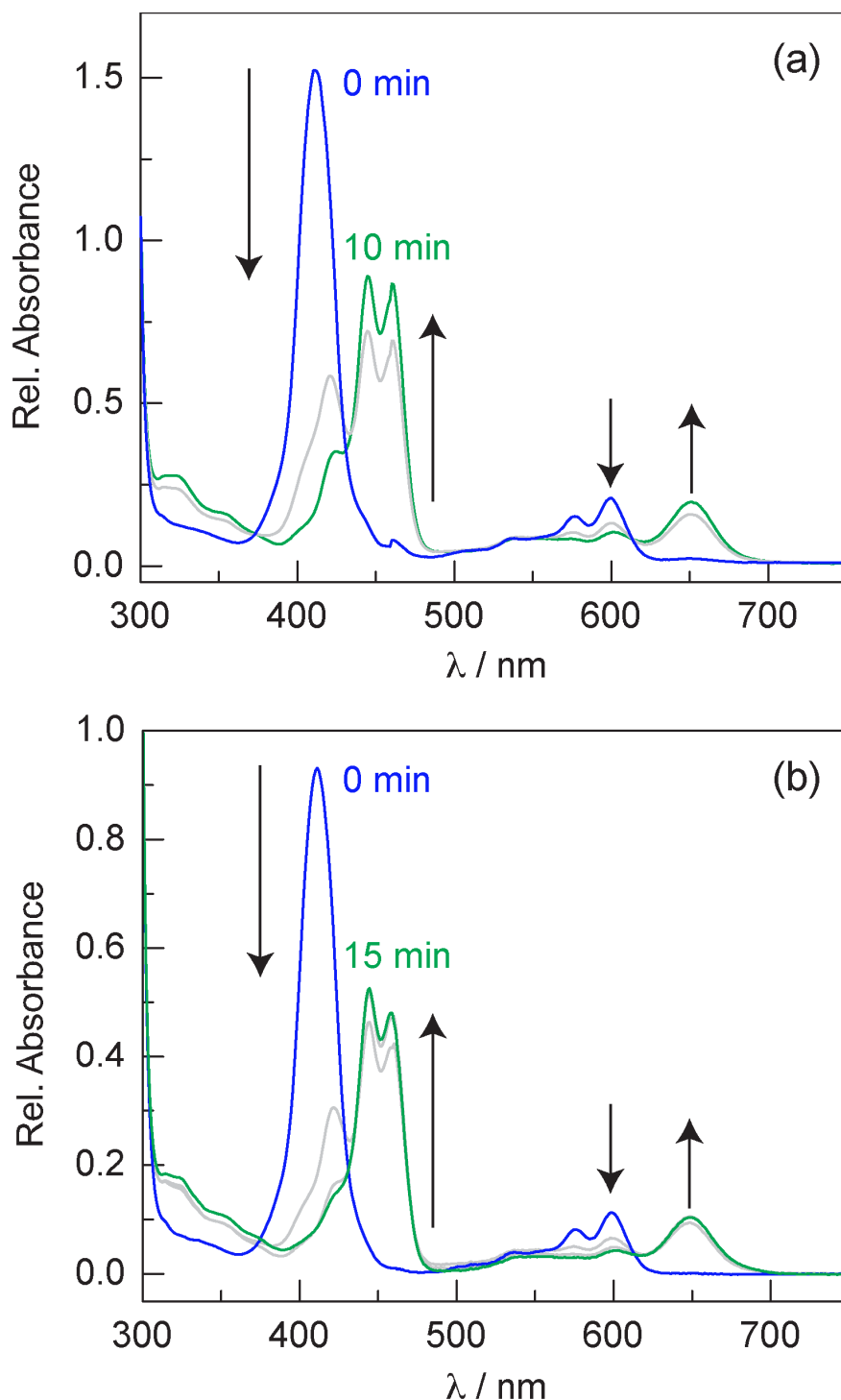


Figure S12. (a) Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in toluene in the presence of 1,3-cyclohexadiene. The initial spectrum of **2** (—) evolves to that of **1** (—) over the course of 10 min. Spectra were recorded every 5 min. (b) Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in benzene in the presence of 1,3-cyclohexadiene. The initial spectrum of **2** (—) evolves to that of **1** (—) over the course of 15 min. Spectra were recorded every 5 min.

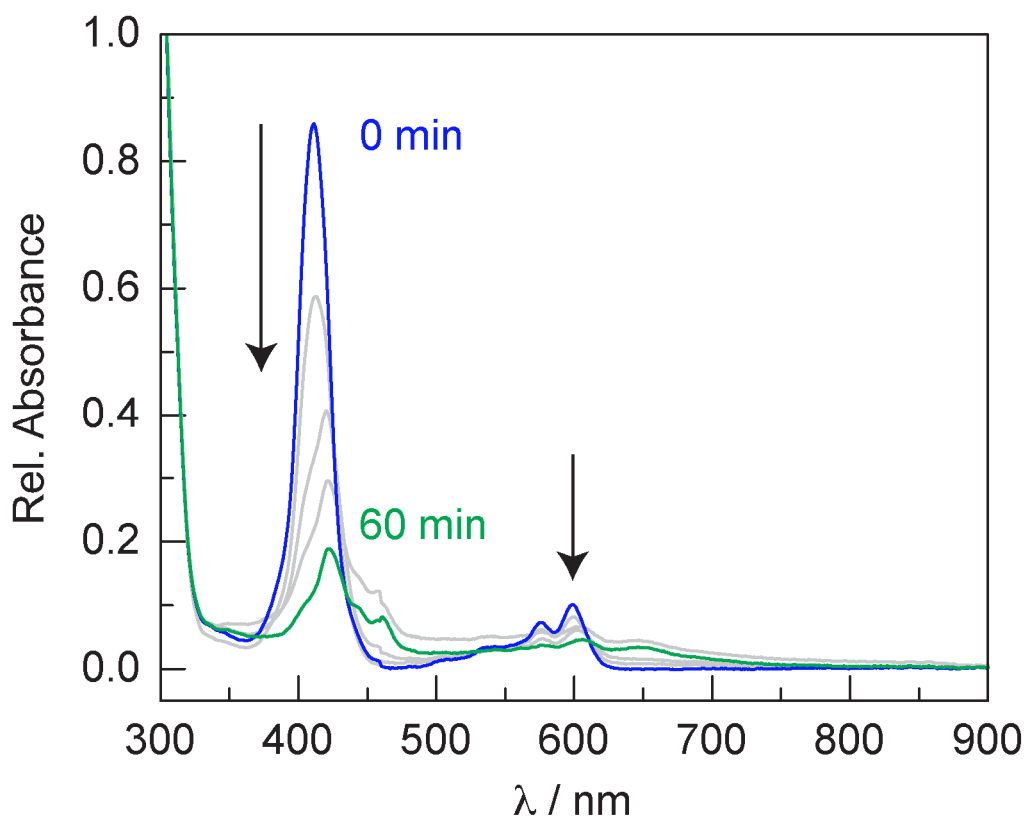


Figure S13. Photolysis ($\lambda_{\text{exc}} > 305 \text{ nm}$) of a sample of **2** in benzene. The initial spectrum of **2** (—) evolves over the course of 1 h (—). Spectra were recorded every 15 min. Given the high BDE of benzene (112.9 kcal/mol), photogenerated radicals react with the weaker C–H bonds of the corrole, resulting in decomposition of **2**. This result indicates that benzene is an unreactive substrate.

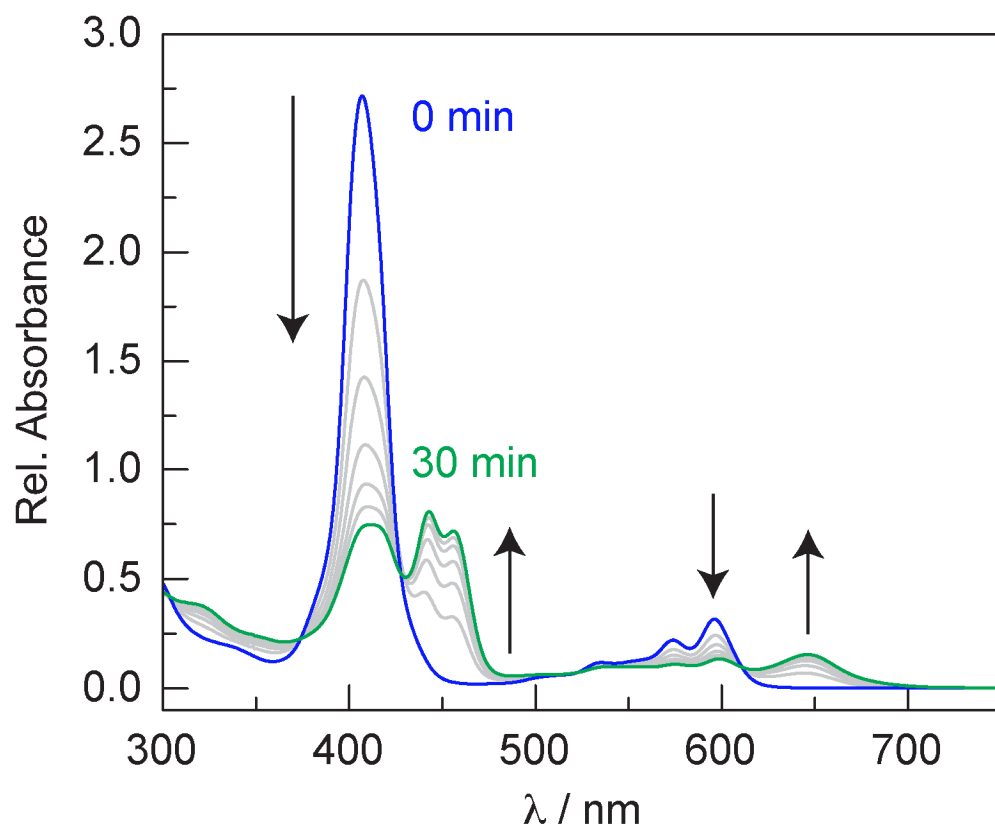


Figure S14. Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in THF. The initial spectrum of **2** (—) evolves to that of **1** (—) over the course of 30 min. Spectra were recorded every 5 min.

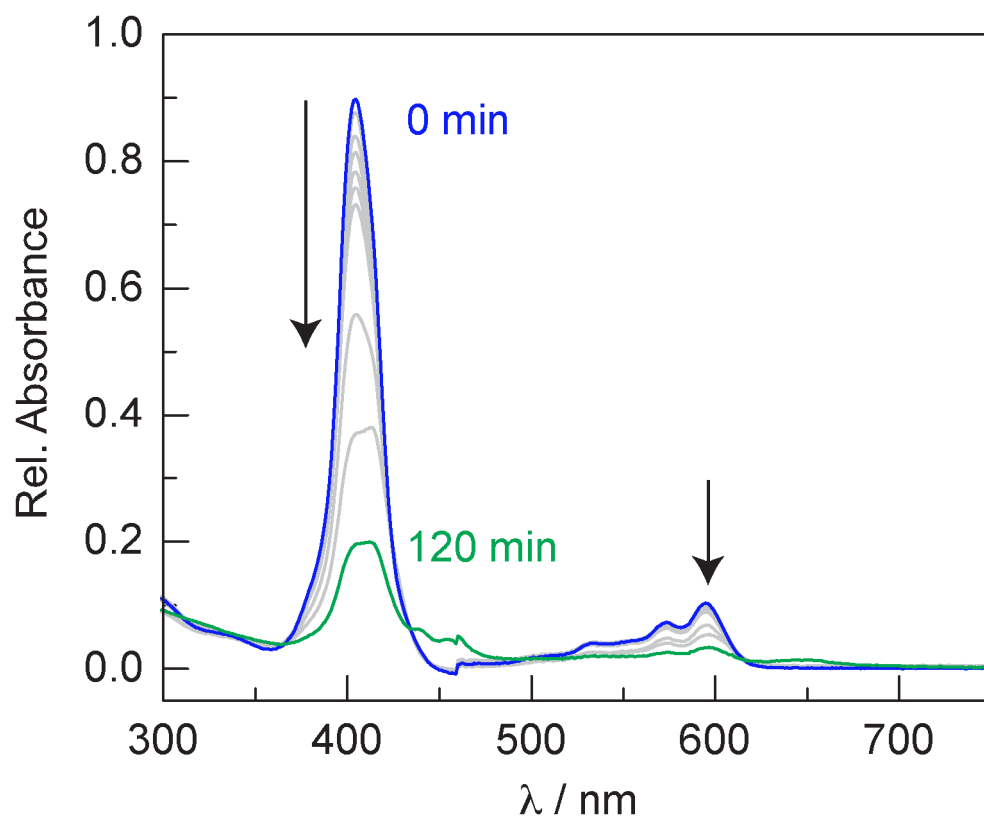


Figure S15. Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in MeCN. The initial spectrum of **2** (—) evolves over the course of 2 h (—). Spectra were recorded every 5 min for the first 30 min, then every 30 min for the next 1.5 h.

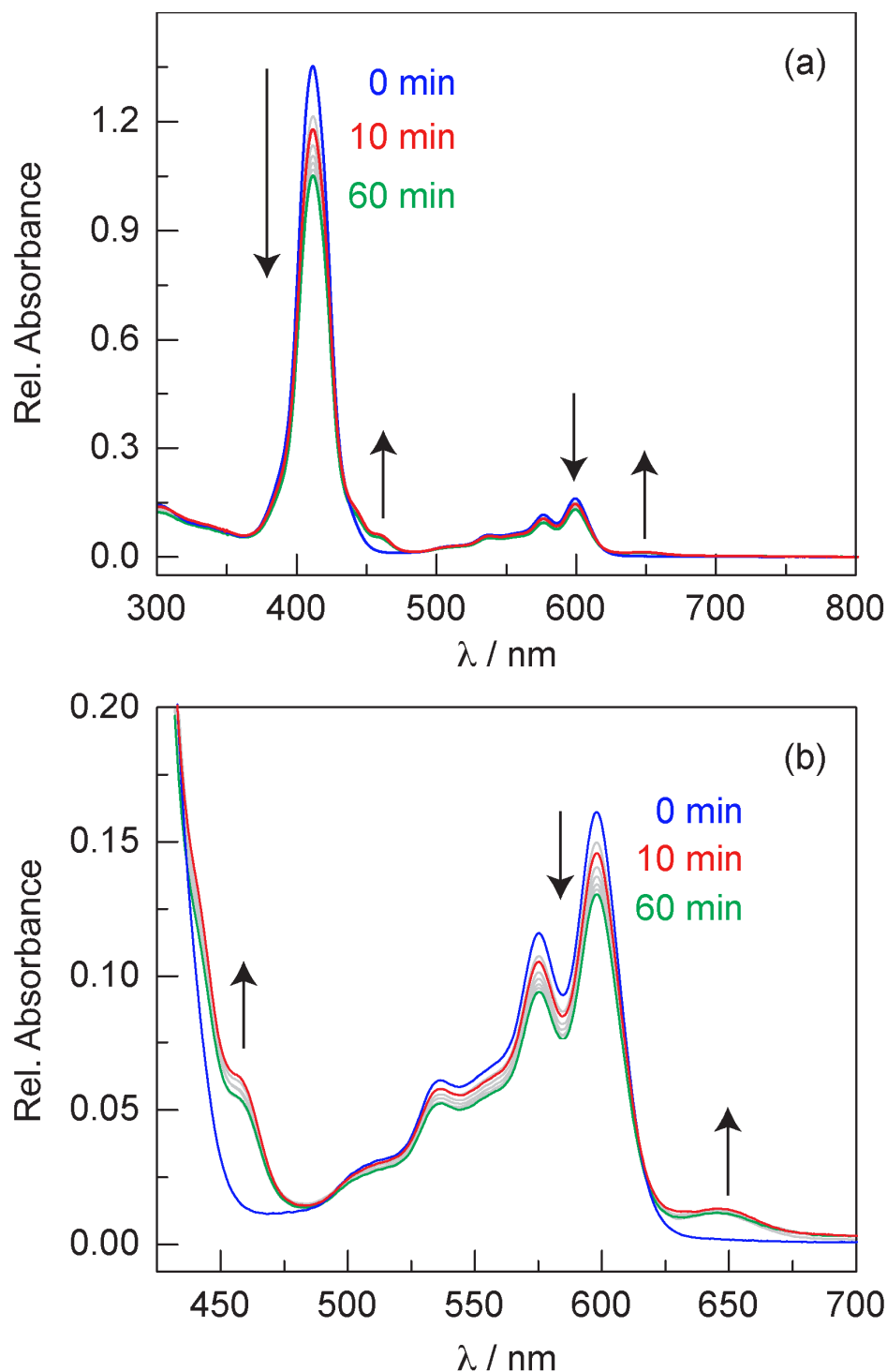


Figure S16. (a) Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in a 1:1 mixture of benzene and 2-propanol. The initial spectrum of **2** (—) evolves over the course of 1 h (—). Spectra were recorded after 5, 10, 20, 30, 40, 50, and 60 min of photolysis. After 10 min (—), the photochemical generation of **1** ceases and the total signal of the sample decreases with subsequent photolysis. (b) Expansion of the Q band region to more clearly illustrate the spectral changes in (a).

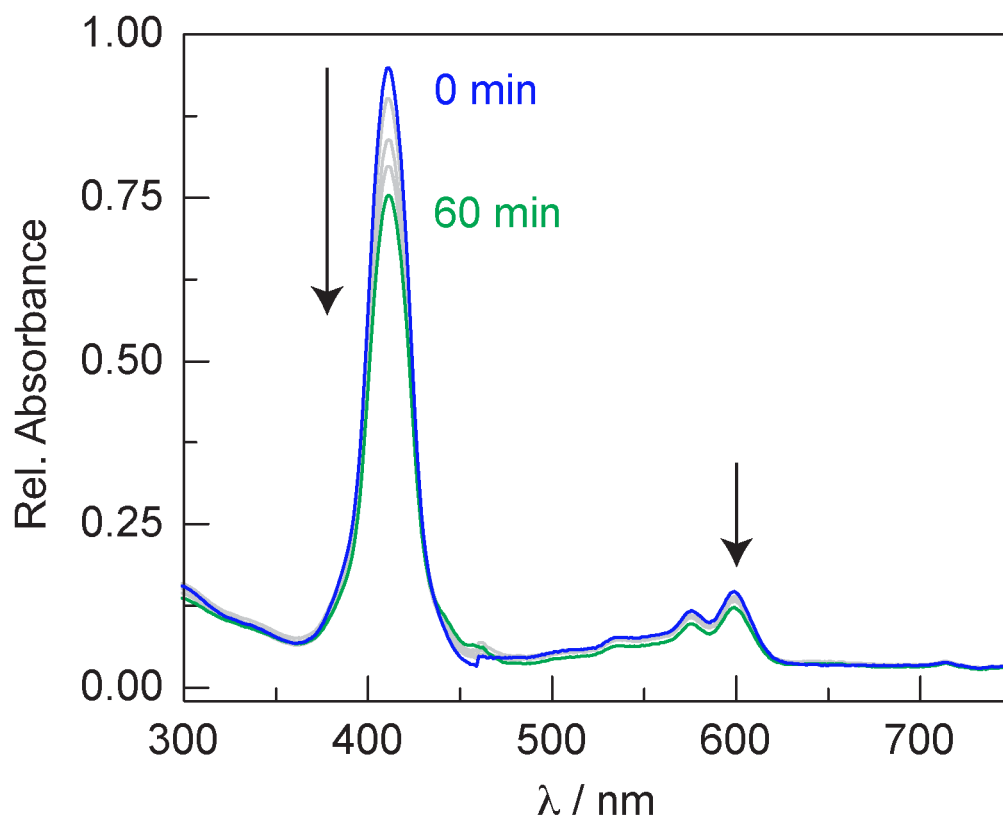


Figure S17. Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in a 1:1 mixture of benzene and cycloheptane. The initial spectrum of **2** (—) evolves over the course of 1 h (—). Spectra were recorded every 15 min.

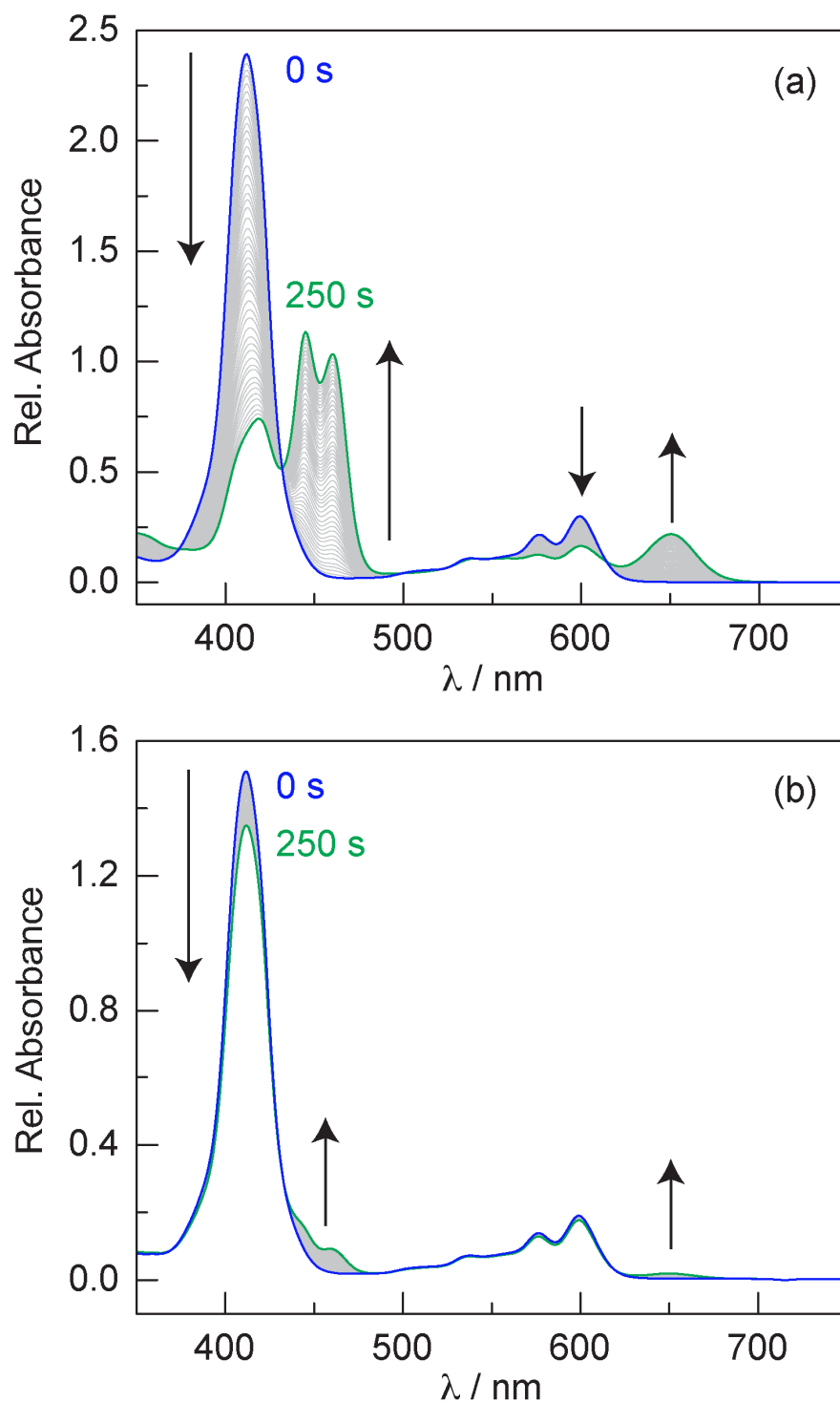


Figure S18. Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in (a) protic toluene and (b) toluene- d_8 . In both cases, the initial spectrum of **2** (—) evolves over the course of 250 s (—) and spectra were recorded every 5 s. After 250 s, the conversion to **1** is 50% complete in protic toluene, but only 7% complete in toluene- d_8 .

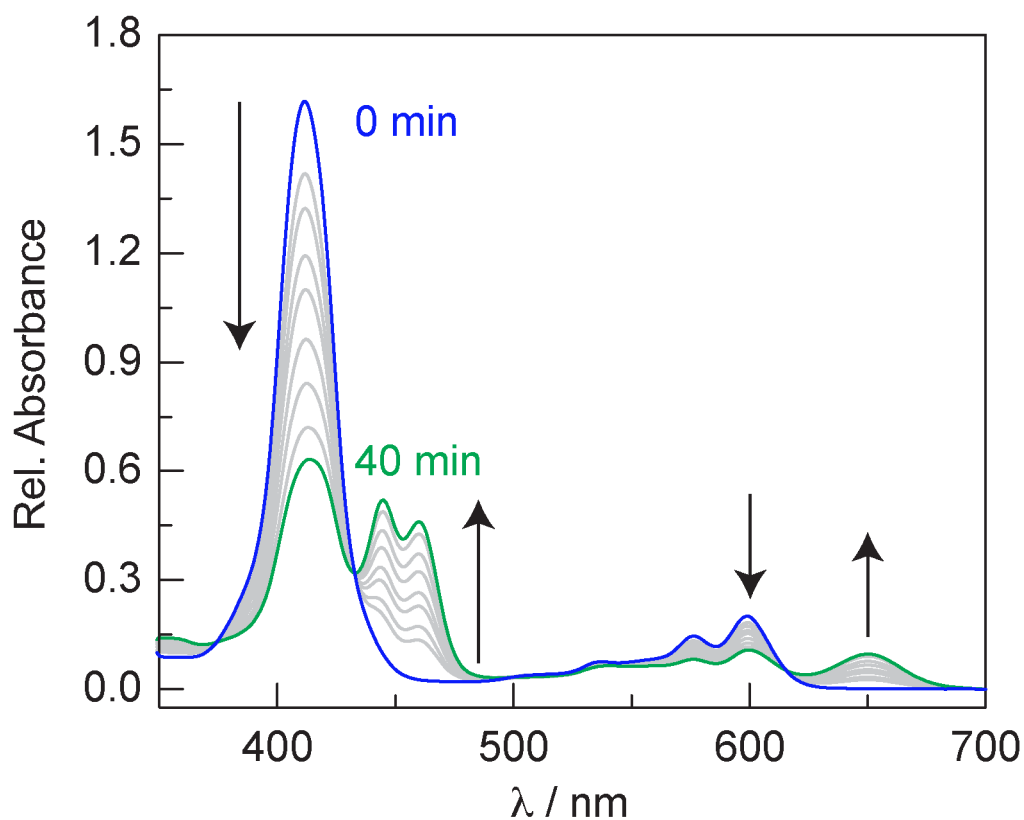


Figure S19. Photolysis ($\lambda_{\text{exc}} > 305$ nm) of a sample of **2** in toluene-*d*₈. The initial spectrum of **2** (—) evolves over the course of 40 min (—). Spectra were recorded every 5 min. After 40 min, the conversion to **1** is 32% complete.

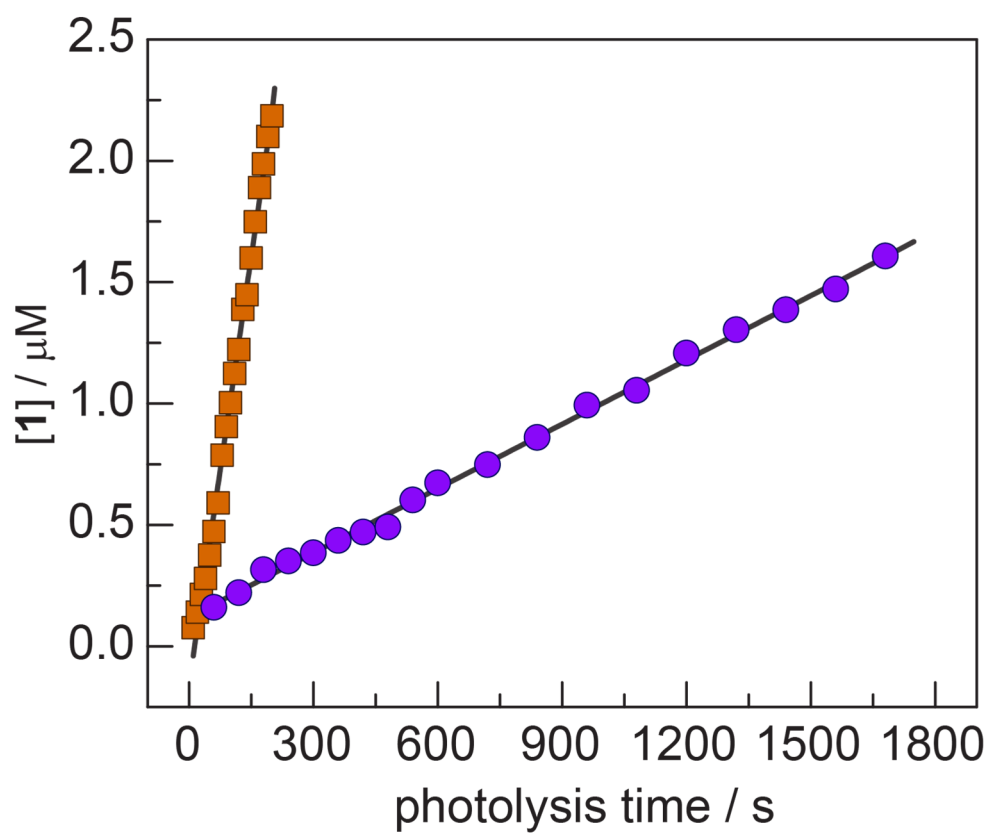


Figure S20. Conversion of **2** to **1** in protic (■) and deuterated (●) toluene as a function of photolysis time, monitoring the growth of the absorption at 650 nm. This data yields rate constants of $k_{\text{obs}} = 1.17 \times 10^{-8} \text{ M s}^{-1}$ for protic toluene and $k_{\text{obs}} = 8.83 \times 10^{-10} \text{ M s}^{-1}$ for deuterated toluene.

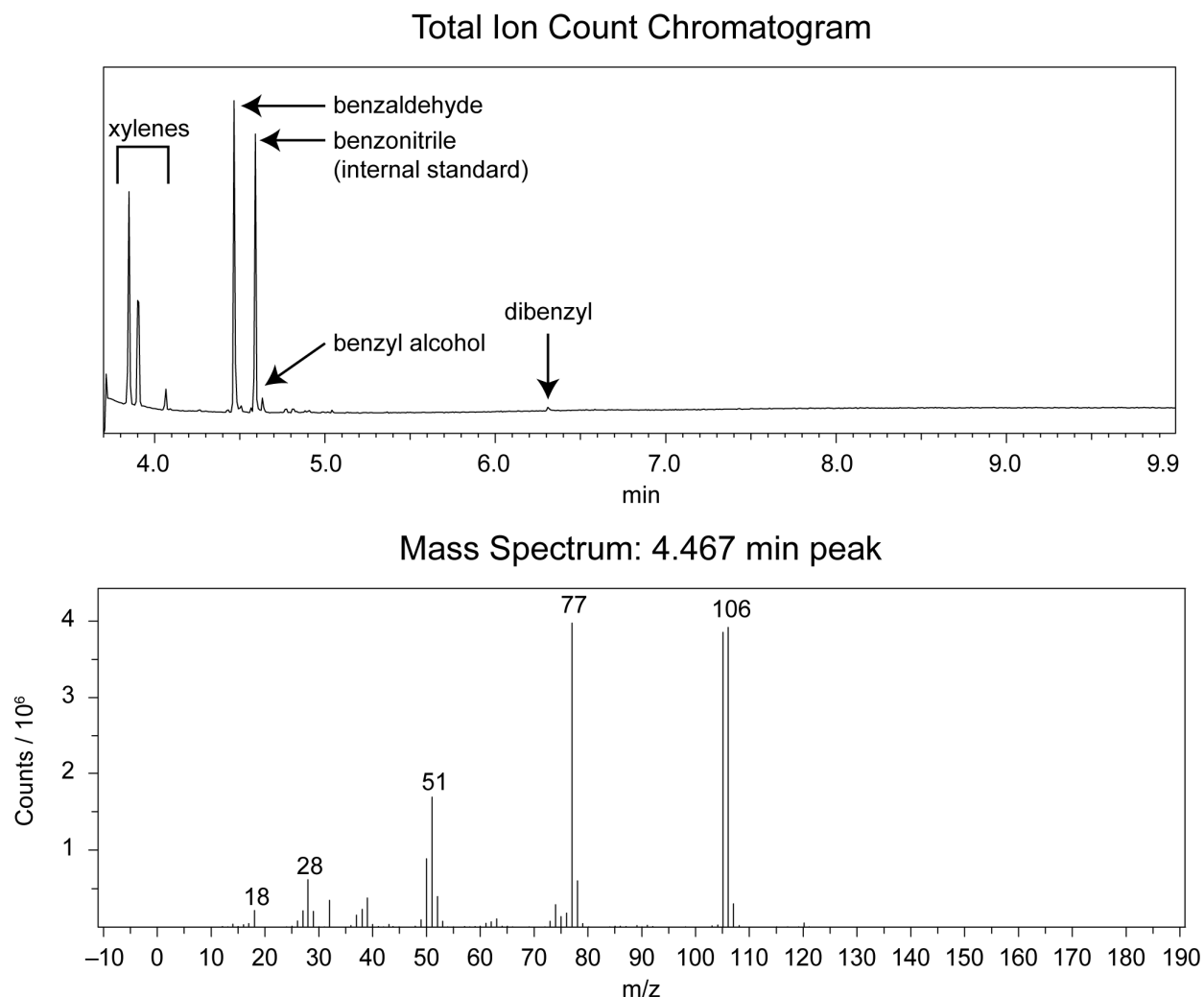


Figure S21. GC-MS analysis from a sample of **2** that was photolyzed ($\lambda_{\text{exc}} > 305$ nm) in toluene. The top trace shows the total ion count chromatogram. The observation of xylenes in the sample is due to the presence of these species in the toluene solvent. Benzaldehyde (peak at 4.47 min) was identified on the basis of the mass spectrum (lower trace) and confirmed by running a standard of the compound.

Table S1. Summary of Crystallographic Data for Compound **2**

2	
Formula	C ₁₀₆ H ₆₂ F ₂₀ N ₈ O ₆ Sb ₂
Weight (g/mol)	2167.13
Temperature (K)	100(2)
Crystal System	Monoclinic
Space Group	P2 ₁ /c
Color	Red
a (Å)	14.7806(17)
b (Å)	19.611(2)
c (Å)	32.180(4)
α (°)	90
β (°)	100.277(2)
γ (°)	90
V (Å ³)	9177.8(19)
Z	4
No. Reflections	38130
No. Unique Refl.	6846
R _{int}	0.1222
R1 ^a (all data)	0.1223
wR2 ^b (all data)	0.2333
R1 [(I > 2σ)]	0.0818
wR2 [(I > 2σ)]	0.2031
GOF ^c	1.023

^a $R1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$. ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$. ^c $GOF = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ where n is the number of independent reflections and p is the number of refined parameters.

Table S2. Cartesian coordinates for the DFT optimized geometry for **2** monomer
(E = -2944.33442498 hartrees)

	<i>x</i>	<i>y</i>	<i>z</i>
C	0.69485168	-3.75067150	0.12409106
C	1.76213544	-4.63395433	0.42261419
C	2.93730843	-3.90054377	0.35871542
C	2.60267666	-2.54940295	0.03404635
N	1.24289056	-2.51600373	-0.12942884
H	1.66519132	-5.67695034	0.68123465
H	3.93154546	-4.26632211	0.56342193
C	3.35996105	-1.36312608	0.00430379
C	2.78833034	-0.08083765	-0.06333189
C	1.24870269	1.59515995	-0.09054017
C	2.54824588	2.17905189	0.02149592
H	4.54026962	1.27590169	0.15327331
H	2.74346928	3.23563747	0.10518703
C	3.47271004	1.16896099	0.04248737
N	1.42127255	0.21553007	-0.15249809
C	0.00432640	2.25119400	-0.08904700
C	-1.24396312	1.60191779	-0.08850930
C	-2.79478704	-0.06220005	-0.04981864
C	-3.46631711	1.19024748	0.10135897
H	-2.71437827	3.24769583	0.21206038
H	-4.52878268	1.30174767	0.25009756
C	-0.72305379	-3.74603221	0.12331649
C	-2.62347689	-2.53245405	0.03633804
C	-2.96584421	-3.88155959	0.36156706
H	-1.70452591	-5.66566765	0.68312973
H	-3.96187977	-4.24101169	0.56859032
N	-1.26362586	-2.50800182	-0.13176082
N	-1.42953778	0.22636611	-0.17043161
C	-2.53379110	2.19297267	0.08208632
C	-1.79538436	-4.62234773	0.42362418
C	-3.37357443	-1.34158708	0.01694802
C	-4.85514864	-1.43648197	0.15726926
C	-5.69907577	-1.24959744	-0.93792029
C	-5.45676255	-1.72519167	1.38205347
C	-7.08012933	-1.34448150	-0.82548289
C	-6.83495548	-1.82931412	1.51741164
C	-7.64822598	-1.63682811	0.40795989
C	0.00037535	3.74692234	-0.03743145
C	-0.40537785	4.49188407	-1.15268606
C	0.39158240	4.42622664	1.12357230
C	-0.41541246	5.88020087	-1.10856033

H	-0.70443136	3.97749994	-2.05835539
C	0.38178089	5.81581630	1.17085004
H	0.69457020	3.86067992	1.99701949
C	-0.02181540	6.55253078	0.05245366
H	-0.72294554	6.45956725	-1.96998189
H	0.68112920	6.33177586	2.07325832
C	4.84242630	-1.46812791	0.12875207
C	5.45443644	-1.74251448	1.35158766
C	5.67583748	-1.30819934	-0.97853967
C	6.83294921	-1.85770230	1.47393400
C	7.05714198	-1.41437217	-0.87929169
C	7.63584784	-1.69154247	0.35272629
F	-7.86394016	-1.16086499	-1.89289672
F	-8.97362205	-1.73293674	0.52728016
F	-7.38315649	-2.10803119	2.70505390
F	-4.70018302	-1.90998459	2.47326412
F	-5.18171664	-0.96718561	-2.13984998
F	5.14797648	-1.04069904	-2.17926100
F	7.83104709	-1.25558713	-1.95786850
F	8.96155273	-1.79812710	0.45953303
F	7.39134101	-2.12250417	2.66004308
F	4.70758708	-1.90355271	2.45323952
C	-0.05164702	8.04361473	0.04464430
O	-0.40014220	8.71414290	-0.90140430
O	0.35536182	8.57175649	1.21400218
C	0.35788086	10.01099155	1.28906089
H	-0.64807445	10.40164284	1.13154312
H	1.02899900	10.42920583	0.53799096
H	0.70844584	10.24824801	2.29041919
O	0.00143387	-1.06039018	-2.80594731
Sb	-0.00500761	-1.06912605	-0.96048533

Table S3. Cartesian coordinates for the DFT optimized geometry for **2**
(E = -5888.72409771 hartrees)

	<i>x</i>	<i>y</i>	<i>z</i>
C	-3.78762916	-2.83963170	-1.42165508
C	-2.92918069	-3.81677673	-1.00590287
C	-1.59182080	-3.35301305	-1.21672052
C	-0.40764403	-4.02344145	-0.85717846
C	0.88783034	-3.51751554	-1.06010204
C	2.13603043	-4.19355411	-0.90318883
C	3.13072880	-3.36889644	-1.36147140
C	2.53836716	-2.15902193	-1.83588926
C	3.16303940	-1.12167755	-2.54794906
C	2.45702195	-0.06479851	-3.14970847
C	2.88408252	1.00883264	-3.99444846
C	1.76921073	1.75718362	-4.33051351
C	0.65506464	1.15431380	-3.68954353
C	-0.73900991	1.37191518	-3.55637509
C	-1.75730838	2.09693757	-4.22030563
C	-2.97490787	1.57588505	-3.80541400
C	-2.71288605	0.51328012	-2.89024196
C	-3.52938212	-0.53195958	-2.41865972
C	-3.01677876	-1.73718686	-1.90768970
C	-5.00355138	-0.37105215	-2.54103203
C	-5.69022290	0.57776119	-1.78155772
C	-5.46644295	0.29655332	1.98069935
C	-7.06720375	0.73084336	-1.85824929
C	-7.79783889	-0.06130428	-2.73380528
C	-7.14448332	-1.00165884	-3.51993624
C	-5.76671500	-1.14394592	-3.41902547
C	-0.52473048	-5.37362362	-0.22680735
C	-0.13948298	-5.56678321	1.10725990
C	-0.24315516	-6.81872048	1.69926105
C	-0.73335179	-7.90662810	0.97008512
C	-1.11688703	-7.72350457	-0.36271052
C	-1.01211068	-6.46889161	-0.95249825
C	4.64513363	-1.16104459	-2.70326267
C	5.46589477	-0.29575296	-1.97986914
C	6.84948949	-0.33680016	-2.07962054
C	7.44847284	-1.24669394	-2.94040811
C	6.65939071	-2.11023650	-3.68928978
C	5.27690584	-2.05776432	-3.56523621
C	-1.76997370	-1.75654400	4.33080269
C	-2.88468899	-1.00803536	3.99459762
C	-2.45742706	0.06534084	3.14962942

C	-3.16323505	1.12230843	2.54777172
C	-2.53835237	2.15941819	1.83553199
C	-3.13045441	3.36931685	1.36086367
C	-2.13558823	4.19367944	0.90241680
C	-0.88752720	3.51743774	1.05949997
C	0.40805378	4.02310954	0.85659227
C	1.59208781	3.35257999	1.21639840
C	2.92954295	3.81613278	1.00569187
C	3.78780473	2.83894625	1.42173430
C	3.01672314	1.73669047	1.90784370
C	3.52908819	0.53147329	2.41905916
C	2.71239034	-0.51358978	2.89067702
C	2.97416433	-1.57606042	3.80608431
C	1.75644471	-2.09687532	4.22091091
C	0.73832744	-1.37187768	3.55666936
C	-0.65571612	-1.15404478	3.68968374
C	-4.64528371	1.16210594	2.70333556
C	-5.27665603	2.05950084	3.56491556
C	-6.65909633	2.11239772	3.68925123
C	-7.44857047	1.24858126	2.94110298
C	-6.85000369	0.33799625	2.08075873
C	5.00322655	0.37041665	2.54166637
C	5.68993789	-0.57842426	1.78226382
C	7.06688979	-0.73164270	1.85921722
C	7.79742899	0.06041277	2.73494089
C	7.14402526	1.00080884	3.52097881
C	5.76628763	1.14322965	3.41980982
C	0.82780418	9.22590027	-1.65734826
C	1.44181538	11.49866443	-1.44242292
C	0.52539637	5.37313778	0.22594278
C	0.14031446	5.56604776	-1.10821255
C	0.24420446	6.81783697	-1.70048910
C	0.73446708	7.90585084	-0.97151155
C	1.11783595	7.72297877	0.36136640
C	1.01283002	6.46851320	0.95143255
C	-1.44021347	-11.49967642	1.44011290
C	-0.82646652	-9.22683553	1.65564511
N	-1.35489915	0.48424637	-2.70238720
N	1.09877551	0.04469128	-3.02236613
N	1.16200747	-2.26670941	-1.59759386
N	-1.66619614	-2.09326609	-1.80224104
N	-1.16196514	2.26677639	1.59720658
N	-1.09921070	-0.04448129	3.02226379
N	1.35443951	-0.48446039	2.70258294
N	1.66621938	2.09292510	1.80213963
O	0.92358526	0.72502229	-0.41000743

O	-0.92377402	-0.72518895	0.40998350
O	0.50390449	9.42287544	-2.80777093
O	1.31771087	10.18926581	-0.85429860
O	-1.31624779	-10.19008979	0.85237517
O	-0.50250229	-9.42398517	2.80601580
F	5.17338023	2.05720416	4.20040350
F	7.84414200	1.75798904	4.37289480
F	9.12141353	-0.08093922	2.82113353
F	7.69306100	-1.62917567	1.08827665
F	5.02150751	-1.36744031	0.92733602
F	-4.54729177	2.91177407	4.29879384
F	-7.23426390	2.98638851	4.52278119
F	-8.77789066	1.29513095	3.04859626
F	-7.60801084	-0.48644589	1.34653479
F	-4.92581626	-0.60077946	1.14474166
F	-5.02171587	1.36690138	-0.92679647
F	-7.69330421	1.62835355	-1.08721678
F	-9.12185063	0.07991923	-2.81975769
F	-7.84467859	-1.75892438	-4.37171252
F	-5.17388019	-2.05788239	-4.19972047
F	4.54790398	-2.90980830	-4.29973890
F	7.23497358	-2.98357773	-4.52321130
F	8.77783054	-1.29284120	-3.04762717
F	7.60712838	0.48737765	-1.34471332
F	4.92482183	0.60093152	-1.14351810
H	-4.86484619	-2.87161243	-1.38775576
H	-3.19230922	-4.77362288	-0.58577959
H	2.24875576	-5.19973413	-0.53322430
H	4.18347254	-3.59765530	-1.40911174
H	3.89751269	1.18084939	-4.32349737
H	1.74106256	2.63358062	-4.95944195
H	-1.60158473	2.85977346	-4.96748507
H	-3.95111022	1.85598334	-4.17037567
H	-1.30042068	-6.33590281	-1.98861436
H	-1.74199299	-2.63282123	4.95990577
H	-3.89814509	-1.17977158	4.32371003
H	-4.18314987	3.59830549	1.40842229
H	-2.24811822	5.19980093	0.53223350
H	3.19285717	4.77286122	0.58541567
H	4.86503394	2.87076148	1.38799735
H	3.95028687	-1.85619089	4.17123400
H	1.60050990	-2.85955015	4.96821099
H	0.46547535	11.86791283	-1.75863487
H	1.85414359	12.13011936	-0.65933036
H	2.11134581	11.46740196	-2.30277114
H	-0.22846579	4.72455742	-1.68270315

H	-0.04621090	6.96865195	-2.73263664
H	1.49088612	8.56293494	0.93186389
H	1.30099899	6.33573411	1.98761559
H	-1.85208338	-12.13105828	0.65671794
H	-2.11009702	-11.46880126	2.30020109
H	-0.46388735	-11.86871554	1.75659447
H	-1.48990684	-8.56337781	-0.93334915
H	0.04736914	-6.96972613	2.73135022
H	0.22923772	-4.72537497	1.68190725
Sb	-0.13962147	-0.65384077	-1.44549241
Sb	0.13942486	0.65370409	1.44547036

Table S4. TD-DFT Calculations of Singlets for **2** Monomer

State	Energy	Wavelength	Oscillator Strength	Orbital Contributions ^a
S ₁	2.2911	541.16	0.1624	23% HOMO-1 → LUMO+1, 77% HOMO → LUMO
S ₂	2.3596	525.45	0.0338	34% HOMO → LUMO+1, 66% HOMO-1 → LUMO
S ₃	3.0684	404.06	1.2911	33% HOMO-1 → LUMO, 67% HOMO → LUMO+1
S ₄	3.1019	399.70	1.1879	23% HOMO → LUMO, 77% HOMO-1 → LUMO+1
S ₅	3.2798	378.02	0.0086	13% HOMO → LUMO+2, 87% HOMO → LUMO+3
S ₆	3.3991	364.75	0.0024	12% HOMO-1 → LUMO+2, 88% HOMO-1 → LUMO+3
S ₇	3.5366	350.57	0.0012	14% HOMO → LUMO+3, 86% HOMO → LUMO+2
S ₈	3.6133	343.14	0.0177	21% HOMO-3 → LUMO, 79% HOMO-2 → LUMO
S ₉	3.6164	342.83	0.0080	19% HOMO-2 → LUMO, 81% HOMO-3 → LUMO
S ₁₀	3.7048	334.65	0.0233	12% HOMO-1 → LUMO+3, 88% HOMO-1 → LUMO+2
S ₁₁	3.7648	329.33	0.0005	18% HOMO-4 → LUMO, 35% HOMO-8 → LUMO, 36% HOMO-5 → LUMO
S ₁₂	3.8932	318.46	0.0078	33% HOMO-5 → LUMO, 67% HOMO-4 → LUMO
S ₁₃	3.9132	316.83	0.0033	100% HOMO → LUMO+4
S ₁₄	3.9243	315.94	0.0061	100% HOMO → LUMO+5
S ₁₅	3.9378	314.86	0.0019	84% HOMO-7 → LUMO

^a Calculated from the normalized coefficients of the excitation wavefunction: % = $(x_i^2 / \sum x_i^2) \times 100$; transition contributions of < 10% have been excluded.

Table S5. TD-DFT Calculations of Triplets for **2** Monomer

State	Energy	Wavelength	Orbital Contributions ^a
T ₁	1.5267	812.12	95% HOMO → LUMO
T ₂	1.6644	744.94	21% HOMO → LUMO+1, 79% HOMO-1 → LUMO
T ₃	1.9901	623.00	22% HOMO-1 → LUMO, 78% HOMO → LUMO+1
T ₄	2.2411	553.23	97% HOMO-1 → LUMO+1
T ₅	3.0941	400.72	13% HOMO → LUMO+2, 87% HOMO → LUMO+3
T ₆	3.2383	382.87	17% HOMO-5 → LUMO, 32% HOMO-8 → LUMO, 35% HOMO-2 → LUMO
T ₇	3.3251	372.87	13% HOMO-5 → LUMO+2, 18% HOMO-4 → LUMO+2, 51% HOMO → LUMO+2
T ₈	3.3284	372.50	10% HOMO-1 → LUMO+2, 78% HOMO-1 → LUMO+3
T ₉	3.3909	365.64	11% HOMO-11 → LUMO, 11% HOMO-1 → LUMO+3, 67% HOMO-3 → LUMO
T ₁₀	3.4631	358.01	10% HOMO-5 → LUMO, 14% HOMO-8 → LUMO, 53% HOMO-2 → LUMO
T ₁₁	3.5911	345.26	17% HOMO-2 → LUMO+1, 29% HOMO-11 → LUMO
T ₁₂	3.6379	340.82	11% HOMO-5 → LUMO+2, 14% HOMO-4 → LUMO+2, 47% HOMO → LUMO+2
T ₁₃	3.6450	340.15	76% HOMO-3 → LUMO+3
T ₁₄	3.6548	339.24	10% HOMO-1 → LUMO+3, 24% HOMO-2 → LUMO+3, 32% HOMO-1 → LUMO+2
T ₁₅	3.6639	338.39	35% HOMO-2 → LUMO+3, 37% HOMO-1 → LUMO+2

^a Calculated from the normalized coefficients of the excitation wavefunction: % = $(x_i^2 / \sum x_i^2) \times 100$; transition contributions of <10% have been excluded.

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