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Semiconducting Supramolecular Organic Frameworks Assembled from a Near-Infrared Fluorescent Macrocyclic Probe and Fullerenes

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ABSTRACT: We report here a new extended tetrathiafulvalene (exTTF)porphyrin scaffold, that acts as a ball-and-socket receptor for and C₇₀. Supramolecular interactions between 2 and these fullerenes serve to stabiliz 3D supramoleculaorganic framework (SOFs) in the solid state formally comprising peapod-like linear assembliesSOFs prepared via self-assembliesSOFs prepared via self-assembliesSOFs in this way act as "tunable functionalaterials", wherein the complementary geometry of the components and the choice for lerene play cruciables in defining the conductance properties highest electric adonductivity ($\sigma =$ 1.3 × 10⁸ S cm⁻¹ at 298 K) was observed in the case of the aSed SOF. In contrastlow conductivity was seen for the SOF based on pristine 2 (σ = 5.9 ×



10¹¹ S cn¹ at 298 K). The conductivity seen for the chased SOF approaches that seen for other TTF- and fullerene-based supramolecular materials despite the flagt the present systems are metal-free and constructed entirely from neultriang blocks.Transient absorption spectroscopic measurements corroborated the formation of charge-transfer tage (and 2⁵⁺/C₇₀⁵⁻, respectively) rathethan fully charge separated states (i2⁺/C₆₀⁻⁻ and 2⁺/C₇₀⁻⁻, respectively) both in solution (toluene and benzonitrile) and in the solid state at 298 K. Such findings are considered consistent with an ability to transfer charge effectively over long distances within the present SOFs, rather than, for example, the formation of energetically trapped ionic spe

INTRODUCTION

Considerable effort is currently being devoted to the preparation and study of organic conductive materials at support the formation of charge-separated (CS) states controlled manner. Such materialsare also of interestas rudimentarymodels for various biological electron-transfer processes including electron-transport hains in the inner mitochondriamembranewhere a remarkable organization of redox-active elementservesto promote the unidirectional movement of charges across the membrane. To date, a nun the SOFs constructed using purely neutrale., uncharged) of synthetic molecular motifs based on tetrathiafulvalene (TTF) and so-called extended TTF (exTTF) cores have been botential conductive materials ere we report a set of 3D made and studied in an effort replicate the key electrontransfer steps within a confined synthetic organic host systems have also been studied in the contextmolecular electronics. Complementaryelectron acceptors, such as 7.7.8.8-tetracyanoguinodimethan€NQ) and F₄TCNQ.⁶ fullerenes (G, C70, etc.),7,8 and quinone carbenessave been used to control the physicochemical properties of the resulting Received: April 8, 2020 electron donor-acceptoconstructsMore generally supramolecular complexes of With suitable electron donor hosts have also attracted attention for their ability to promote efficientphotoinduced electron-transfer (PET) reactions and stabilize charge-separatedstates. This has made such constructsof interest for solar energy conversion,¹⁰ the

development of organic solar cells,⁻¹³ and the assembly of organic conductive materials¹⁴ A particularly attractive approach to creating electroactive supramoleadastructs is via self-assembly/deally, this allows active functional materials to be prepared through simple mixing under controlled conditions. To date, a number of self-assembled conductive materials have been reported; however, most either consist of 1D arrays^{15,16} or rely on controlled metal coordination chemistr $\sqrt{1-20}$ To the best of our knowledge. electron donor and acceptor species have not been explored as hierarchical fully organic SOFs created from an exTTFporphyrin-based macrocyclic host (2; Figure 1) and fullerenes via a process involving peapod-like self-asseAsbbetailed below, the conductivity of these SOFs can be regulated through the choice of encapsulated fuller \mathfrak{G}_{70} . The

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Scheme 1Synthesis of Receptor 2



best system, a C₇₀-based SOF, displayed an electrical conductivity of $\sigma = 1.3 \times 10^{\circ}$ S cm¹ at 298 K.

recognition sites for complementary spherical guest molecules upling using 4.4'-bipyridineas the template. Following viz. a nanometer-sized hexagonadceptor site above the These unique structurfalatures allow for the self-assembly of 22% yield. Details of the synthesis of 2 are summarized in various superstructureisn the presenceof fullerenes. The saddle-shaped receptoites of 2 act as connectorswhen exposed to complementary spherical or near-spherical fulleranalysis (cfSupporting Information) The structure of was quests. This allows for ball-and-socket1D aggregation. Meanwhile the central hexagonahanospace of promotes supramoleculassembly in the orthogonablirection when architectures the presence offullerenesEvidence of the underlying interactions and overall structures of the twocomponent electron donor-acceptor ensembles formed fromanalyses all cases SOF-like structures are settime crystal 2 and fullerenes G_0 and C_{70} came from single-crystal ray diffraction analysed hese studies evealed that imilar selfassembled 3D supramoleculativorkswere formed in the solid state in the case of both fullerenes. However, small differencesare seen that were expected to translateinto differences nthe bulk electronic features. Studies of the excited-state dynamics both as 1:1 complexes in solution a as extended arrays the solid state provided support for charge-transfe(CT) processes within these systems ather than the formation of charge-separated states as a result of full electron transfer. The presentSOFs show promise as conductive materials ith the system based opporting to be more effective than that based on Co our knowledge, this is the first example where an electroactive system base exTTFs,porphyrins,or fullerenes has been prepared via the stark contrast with conductive materials, such as metal-organic frameworks (MOFs),¹⁷⁻¹⁹ covalentorganic frameworks (COFs),^{21–23} and hydrogen-bonded organiterame-works (HOFs),^{24–26} built up from charged building blocks.

RESULTS AND DISCUSSION

Receptor Design and Synthesis. We envisioned that such systems displawith (2) the strongly electron-donating Sessler group (Figure inset)²⁹ would (3) lead to a neutral SOF with semiconductive properties.test this hypothesis,

an exTTF Zn-porphyrin containing 1,3-dithiol-2-ylidene moieties in the 1,10 positions and m-ethynyl-phenysub-The molecular geometry of 2 serves to define two distinctive ituents in the 5.15 positions was subjected to Glaser-Hay trifluoroacetic-acid-mediated demetalationextended tetra-

central porphyrin and two saddle-shaped arcs at the periphethylafulvalene (exTTF)-porphyrinoid scaffold 2 was obtained in Scheme 1All new compounds were fully characterized Hby and ¹³C NMR spectroscopy as well as massspectrometric further confirmed via single-crystal-ray diffraction analysis (vide inf ra).

Single-Crystal X-ray Structural Studies. The solid-state exposed to Gor C70. As a result, receptor 2 forms infinite 3D geometries opristine receptor 2 and the supramolecular 3D networks stabilized in the presence G_0 and C_{70} were determined via single-crystalX-ray crystallographic structure of 2 determined in the absence affullerene quest reveals a saddle-shaped geometry for the constituent quinoidal porphyrinoid macrocycle that bears resemblance to previously reported monomeric exTTF-porphyrinBy analogy to what was seen for monomeric exTTF-porphyrindistortion from planarity is expected for the receptorsystem 2 (vide inf ra). Howeverin contrast with the simple monomee 1s defined by its large pseudohexagonal macrocyclic core with a diameter of ca.13 Å created by the two constituent exTTF-porphyrins connected via two butadiyne linkers through the metaphenylenerings at the porphyrin meso-positionsFigure 1a,b). This hexagonalcore and the saddle-shapedlefts defined by the exTTF moieties (Figure 1c) provide two distinctive receptosites thatappeared suitable for pherical questrecognition (videinf ra). An analysis of the packing self-assembly of uncharged organic components. This stands in diagrams (Figure 1d,e) revealed that individual units of 2 exist in a slipped-sandwich fashion in the solid state, presumably as a result of various stabilizing noncovalentinteractions. The parallelarrangement of seen in the solid state generates an SOF-like structure characterized by the presence of infinite 1D channels occupied by solvent molecules.

The single-crystaX-ray diffraction analyses the SOFs formed by 2 and fullerenes, and C70 differ from those of combining (1) the well-known template-directed synthesis of pristine 2. In these instances, inspection of the packing diagram cyclic porphyrin oligomersand the guest-inclusion properties revealed a parallstacking of 2 and the presence in the solid state of end-to-end self-assembled supramolecular architectures 1,3-dithiol-2-ylidene guinoidal porphyrin (1) developed in the containing cobound fullerenes within the saddle-like receptor sites (cf.Figure 2a-f). This latter peapod-like arrangement is presumably stabilized via a combination $\sigma f - \pi$, $n - \pi$, $C - \pi$

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Figure 1. (a,b) "Ball-and-stick" and "superimposed space-filling" model of receptor 2 showing the large hexago (rail Vriew dasidy education) to highlight the saddle-shaped clefts defined by the exTTFs within the porphyrin dimer 2. (d,e) Illustrative examples of the intricate supramole packing seen for 2. Residual solvent molecules) (64:102: the voids and other disorders at terminal propyl groups are omitted for clarity. Inset: Chemicastructures of the monomeric exTTF-porphyrin reference system exTTF-porphyrin dimer.

H••• π , concave-conveand electronic (D-A) interactions. Fullerenes are also encapsulated inside the pseudohexagonadonalcavity under these experimentadonditions. On the core defined by receptor 2. This allows for noncovalent fullerene-receptor contacts thextistperpendicular to those defined by the exTTF-derived cleftshe net result of these orthogonaball-and-socket-like supramolecular interactions the formation of self-assembled 3D-SOFs (Figure 2g,h).

While differences are seen, the gross structures (space groppectral signature becomes broad. This may reflect the Fddd), unit-cell dimensions (86 735 Å³ for (2•C 60) n versus 91 283 Å³ for $(2 \cdot C_{70})_{n}$ -based SOFs)and overall electron donor-acceptor stoichiometries are similar irrespective of the upramolecular complex with 2 (i.e., 2000 may contribute fullerene used (vi \mathfrak{L}_{60} or C_{70}). However, it is speculated that C₇₀ being a unique egg shapeight overlap more effectively with the TTF-derived saddle-like cleft in 2 than its spherical We therefore focused on absorption-and emission-based congenerC₆₀ A distinctive edge-on binding within the saddle techniquesto quantify the host-guestinteractionsin the and pseudohexagonal core of receptor 2 is observed in the satisfiestion phase (vide inf ra). of C70 (Figure 2b vs 2e). This is also reflected by the comparatively higher conductivity value of the C70 SOF compared with that of G analogue (vide inf rat) should be noted that the fullerenes themselves are highly disordered ininteractions with Go and C70 were explored in solution the these SOFs. Even synchrotron X-ray radiation did not improve/vis-NIR spectra of receptor 2 recorded in toluene and the data quality of these crystals, which is thought to be due benzonitrile resemble those of the construction 1; however, within these SOFs. However, the nature of host-guest binding an internal charge transfer (ICT) from the electronbetween receptor 2 and fullerenes is fully established.

¹H NMR Spectroscopic Titrations. To probe the hostguest interactions in solutidid,NMR spectroscopic titrations of 2 with Go were performed in tolueneed 298 K. Upon the incrementaldition of up to 10 equiv of C to a solution of 2, gradualdownfield shifts in the meso-phenylengeroton resonances at 7.39 ppm ($\Delta\delta$ 0.47) and 6.18 ppm ($\Delta\delta$ 0.07) were observed (See Figure S20.) This observation is

consistent with G complexation occurring in the pseudohexcontrary the terminabroton signals in the aliphatic region of the spectrum (ascribed to the propyl groups) do not undergo a noticeable shiftWe interpret this latter finding in terms of the isC_{70} not being appreciably bound within the exTTF saddles. Upon the addition of increasing quantities fullerene, the

generation of open-shellspecies a result of partial CT interactions. However, the poor solubility of C₇₀ and its to this broadening. These solubility problems precluded the use of NMR spectral methods for quantitative binding studies.

Photophysical Studies. As a predicate to exploring the potential conductivity properties of the previously described SOFs, the solution-phasespectral features of 2 and its the absence of metal atoms and the presence of large 3D voids, the absorption band in the 650 to 670 nm range, ascribed donating 1.3-dithiol-2-vlidenenoieties to the porphodimethene cores enhanced (Figures S28 and SO)-vis-NIR spectroscopic titrations 2 with fullerenes in toluene and benzonitrile were carried outlese revealed guenching of the broad Q-like ICT absorption band at 655 nm in toluene and 667 nm in benzonitrile (shown for the Gensemble in Figure 3b,c; see Figures S33 and S35 for ensembles along with subtle red shifts of and 10 nm in toluene and benzonitrile,



Figure 2. (a-c) Simplestunit of an electron donor-acceptor ensemble and C₆₀ (d-f) Corresponding subunfor 2 and C₇₀. The two orthogonal ball-and-socket receptor-fullerene interactions referred to in the main text involve fullerene binding to the saddle-like clefts on the and the pseudohexagonal core above the porphyrine sinestively (h) Truncated structure of the 3D SOF with empirical formula (2.C produced via the self-assembly of receptor 2,0 and 0 were along the crystallographic "x" and "z" axes, respectively. A similar SOF is formed in the case of G see the Supporting Informationset: Calculated molecular dimensions of C respectively determined from X-ray structuradata Note: Residuadolvent molecules isorder in the terminal ropylgroups and fullerene moleties are omitted for clarity.

respectivelyAs suggested by a refereentrol titrations of1 with C_{60} were carried in benzonitring appreciable changes were seen in either the absorption or the fluorescence spectsubstantiabss of the spectraltensity. This emission feature (cf. Figures S36 and S45).

The spectrachanges seen in the case20 are ascribed to intermolecular CT interactions between the electron-donatir host, 2, and the electron-accepting fullerenesth in their ground state. The spectral titration of 2 againsta chemical oxidant,viz.tris(4-bromophenyl)-ammoniumhexachloroantimonate ("Magic Blue"), revealed similaspectralfeatures. This evolution was interpreted in terms the generation of $2^{(*+)2}$ followed by $2^{(2+)2}$ via two single-electron and doubleelectron oxidationsrespectively with an appreciable color change (Figures S30 and S31) Analogous spectrahanges were observed via spectroelectrochenaicalyses when the voltage was stepped up from +0.0 to +1.0 V in benzonitrile (Figure 3a).

the 550-750 nm region but exhibits a significant NIR emissionetalated form of 1, where weak interactions were seen for with a maximum centered at 808 ngr=(1660 nm) in toluene (Figure 3d). This finding is rationalized in terms of a photoinduced ICT from the 1,3-dithiol-2-ylidene moieties to the porphodimethenecore. Independentsupport for this suggestion came from the facthat an increase in solvent

polarity from toluene to benzonitrile leads to a marked 42 nm red shift in the fluorescence maximum accompanied by a was gradually guenched and blue-shifted from 808 to 806 nm when 2 was titrated with fullerenes in toluene for ure 3e,f ¹Gind Figures S40 and S42). These spectral changesare rationalizedin terms of a shift in the CT deactivation pathways, that is, an exTTFporphyrin-to-fullerene CT transition with an energy of 1.6 eV (Figures S38 and S43) rather than a 1,3-dithiol-2-ylidene-to-porphodimethene ICT

pathway with an energy of 1.83 eV. The binding constants *K* corresponding to the interaction of 2 with C_{60} or C_{70} are on the order of 100^{-1} in toluene at 298 K, as derived from the steady-state spectroscopic titrations. Here, good correlations a 1:1 binding isotherm, but not other common fitting models, were seen (Figures S3334, Receptor 2 fails to show any noticeable fluorescence within 39, and S41). On the basis of our prior studies of the

 $Li^+@C_{60}$ in the absence of an anion, we hypothesize that the binding predominantly involves the interaction of the fullerene with the pseudohexagonabre presentn 2 rather than the peripherasaddle-like binding sitesupport for this inference came from the qualitative analysistbe spectrashifts seen

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Figure 3. (a) Spectroelectrochemical oxidation of 2 in benzonitrile um figas Blue supporting electrolyte. At the reference electrode, Pt as the counter electrode, and a Pt mesh as the working electrode. (b,c) Results of UV-vis-NIR spectroscopic titrations of 2 (kept constant × 10⁻⁶ M) with C₇₀ in toluene and benzonitrite spectively 298 K.Note: The absorption spectra of the fullerenes were subtracted from the original spectred) 3D-NIR emission spectrum of 2 in toluenteenges in the NIR emission of 2 (kept constant at f M) observed upon titration with G_0 (e) in toluene (660 nm excitation) and (f) in benzonitrile (670 nm excitation) at 29 b Ke. The G_{cr} based emission was subtracted from the originadectra to highlight the changes.

upon the addition of C₇₀ to toluene-d solutions of 2, as previously discussed.

2 and its corresponding G-bound formswere carried out both in solution (cf. Figure 4a-f) and in the solid state (cf. Figure 4g-i). The raw data were analyzed using Global Targeoverall dynamics albeit only slightly (Figure S48a-i and Analysis (GloTarAn) by implementing a model based on the Tables S4 and SO the contrary reatment with more than information obtained from steady-stateneasurementecf. Figure S51a). The photoirradiation of 2 in toluene or benzonitrile at 676 nm in the absence of fullerene gives rise to a broad absorbance feature at 555 nm and a sharp negativesorptions of free and uncomplexed OGo. No evidence of feature at 670 nm ascribed to ground-state photobleaching (Figure 4a). This promptly formed transient state is assigned basis of the previously described studies, infer that charge to a vibrationally hot, excited CT state, **[(1,3-dithiol-2-ylidene)^{δ^+} (porphodimethene)^{δ^-}], abbreviated as **- $(exTTP^{5+}H_2P^{5-})$. It transforms within 5.3 ps in toluene and 5.48 ps in benzonitrile into a relaxed beit still excited CT state: *(exTT $\mathbf{\tilde{P}}^{+}$ •H $_{2}\mathbf{P}^{\delta^{-}}$). Hand-in-hand with the relaxation is a blue shift in the excited-state absorption features across the journal state absorption state absorption features across the journal state absorption state absorption features across the journal state absorption state absorption state absorption state across the journal state absorption state absorption state across the journal state absorption state across the journal state across visible region. At a delay of 100 ps, the dominant species is the sorptions at 1100 and 1450 nm, respectively. H₂Pcharge-separated state, $(exT^{-}H_2P^{-})$, as inferred by a 490 nm maximum and a 447 nm shoulde(Figure S27a)both features decay with a halife of 750 ps. In the case of the 2*fullerene complexes,the GloTarAn is based on the coexistenoé (exTTF+•H₂P^{δ-}) and (H₂PexTTP⁵⁺•fullerene⁵⁻) and assumes their simultaneous photoexcitation³³ (Figure S51b). As far as the excited *- $(exTTF^{\delta+}H_2\dot{P}^{\delta-})$ is concerned on a time scale of δ -10 ps, a paralleldecay is seen when 6 or C₇₀ is present In both casestwo initial products are formed orresponding to the charge-separated (exTTfH $_2P^-$) and the excited *(H $_2P^-$) $exTTP^{+}$ -fulleren e^{-}) states respectively the ground state is then quantitatively recovered within a few hundreds of picoseconds. The CT state, $(H_2P-exTTP^{+}-fullerene^{\delta})$, exhibits excited-state characteristic feature \$45 and 900 nm as well as fingerprintabsorptions $C_{60}^{\delta^-}$ at 1072 nm (Figure S47a-c) and of \mathcal{R}^{δ^-} at 1380 nm^{4,35} (Figure 4d-i).

These species decay with lifetimes of only a few tens of picosecondsOn longer time scales that is, >3000 ps, the Transient absorption spectroscopic (TAS) studies of pristine plet excited state of C₇₀ is the only discernible species; presumably his is the product of the ground-state recovery of (H₂P-exTTF+•fullerene). The solvent polarity impacts the

4 equiv of the chemical oxidant Magic Blue (Figure S49a-f) in benzonitrile gives rise to features similar to those recorded for the chemically oxidized form of 2 and the singlet excited CT or electron transfer is seen under these cond@iorthe hopping would be feasible within the $(2_{6}^{\circ} \mathbb{Q}_{n})_{n}$ and $(2 \cdot C_{70})_{n}$ SOFs in the solid stateln both cases the transients which appear immediately after excitation of solid same those observed in solution for (H₂P-exTTP⁺-fullerene^{δ^-}) although red shifts are se $\mathfrak{G}_{0}^{\delta^-}$ (Figure S50a,b) and $\mathfrak{G}_{0}^{\delta^-}$ exTTP⁵⁺•fullerene⁵⁻ shows a biphasic decay with shoathd long-lived components Figure 4i and Figure S50c). Two different (H₂P-exTTP⁺•fullerene⁻) speciesare seen, as inferred from the crystpacking. The short-lived components of 24.5 and 14.5 ps for the C_0 and C_{60} SOFs, respectively, mirror what is seen in solution as previously note and, by analogy, are assigned to CT interactions involving the fullerenes directly bound to The long-lived components of 750 ps and 2.2 ns seen for the and Co SOFsrespectively, may reflect CT interactions between a cobound C_{70} and an exTTF subuniteven though these are rather distant from one another.

Density functionalheory (DFT) calculations (M06-2X/6-31G^{*})³⁶ on pristine 2 (Figure S52) and encapsulated species with fullerenes bound in all recognition sitemely $2 \cdot (C_{60})_3$ and $2 \cdot (C_{70})_3$, were carried out (Figures S53 and Sb4) he case of the pristine receptorboth the HOMO and LUMO



Figure 4. Solution and solid-state excited-state dynamics of 2 a) d\$20 Es as inferred from femtosecond-TAS pump-probe studies (λ 676 nm,360 nJ) carried out at 298 K using sevtimed delays between 1 and 5500(a) Differential absorption spectra of 2 in tolue(te). Deconvoluted species-associated spectra (SAS) in toluene with **($\pm \chi PF$) (SAS1,pink), *(exTTF⁵⁺•H ₂P⁵⁻) (SAS2,light green) and (exTTF⁺•H ₂P⁻) (SAS3, brown), obtained via target analysis in GloTarAn. (c) Population dynamics of SAS1 (5.30 ps), SAS2 (111 ps), and SA (860 ps), along with the residuals of the fit. (d) Differential absorption spectra ($\mu_2 P^{5-}$) (SAS1,pink), (H₂P-exTTP⁵⁺•C₇₀⁵⁻) (SAS2,navy),(exTTF⁺•H₂P⁻) (SAS3,brown), and *C₇₀ (SAS4green) obtained via target analysis in GloTarAft. (g) Differential absorption spectra ($\mu_2 C_{70}$) SOF crystals(h) Deconvoluted SAS with short-lived₂(HexTTP⁵⁺•C₇₀⁵⁻) (SAS1, navy)ong-lived ($\mu_2 P$ -exTTP⁵⁺•C₇₀⁵⁻) (SAS2, orange), and C₇₀ (SAS3, green) obtained via target analysis in GloTarAn. (i) Population dynamics of SAS1 (24.5 ps), S2 (750 ps) and SAS3 (>10 ns) on spilong with the residuals of the fit.

are essentially delocalized on the exTTF-porphyrin molecular complexes afind $C_{60}C_{70}$ the HOMO and HOMO-1 are also mainly located on the exTTF porphyr-1d,e).DFT calculations support this finding,that both the ins. In contrast, the LUMO, LUMO+1, LUMO+2, and LUMO +3 are predominantlylocated on the fullerenes.Natural transition orbital (NTO) analyses of the S₁ states of both 2•(C₆₀)₃ and 2•(C₇₀)₃ were also carried out; the results proved to be consistent with the proposed exTTF-porphyrin-along the crystallographic "z" axi8/sing the same setupa to-fullerene CT inferred from the TAS experiments previously uther ca. 2 order of magnitude enhancementin the described (Figure S55).

Single-Crystal Conductivity Studies. In light of the for measurements again made along the crystallographic "z" long-range order seen in the solid state expected that the axis, single crystals $(2 \cdot C_{70})_n$ gave rise to a conductivity of 1.3×10^{-8} S cm⁻¹ at 298 K. An effort was made to analyze fullerene-containing SOFsased on 2 would prove to be conductive. To test this propositisingle-crystal conductivity crystals of (2 • C 70) perpendicular to the crystallographic "z" measurementswere performed using a "wire-paste" twoaxis (i.e., crystallographicx" or "y" axis). Although some contactprobe approach (see Figure 5, inset). Because of evidence of ower conductivity was obtained he very short the inherent shapes of the crystals as well as their fragile nature tact of the probes coupled to an uncertain cross-section did we were only able to obtain reliable data for the conductivity not allow reliable conductivity values to be derived. In all of the along the crystallographic "z" algorithms low conductance (σ = systemsconsidered hereno increase in conductivity was 5.9×10^{-11} S cm⁻¹ at 298 K) was observed in the case of observed upon photoirradiation. pristine 2 along this axis. We interpret this finding in terms of aTheoretical studies also provide support for the experimental lack of induced electronic communication between neighbor-finding that the conductivities of the fullerene-based SOFs ing subunitsThis might be due to the parallel arrangement of should be higher than those of pristineThe analysis of the



Figure 5.(a) Current versus voltage plots with linear fits of the electrical ctivity data for 2 and the structurally characterized SOFs of this study (i.e., (2.6), and (2.C70), respectively). (b) Average conductivity values (left set of columns) and best performance (right set of columns) obtained from single-crystanductivity studies of (2+C 60)n, and (2+C70)n, respectivelyunder ambient conditions in the danset: Optical images ofhe two-contact probe device made from single crystals (2fC 60), and (2·C70), respectively, sing the probe-paste approach. Electrical conductivities were measured along the crystallographic "z" axis at 298 posed conductivity paths for (2) Cand (2·C₇₀) n respectivelypassing along the crystallographic "z" assignment from a combination of FT calculations (see the text) and single-crystal structurabnalyses (provided for ease of visualization).

putative electron-transfeathway along the "z"axis of the crystal structures of $(2 \cdot C_{60})_n$ and $(2 \cdot C_{70})_n$ revealed a systematic zigzag pattern that close to identical in both structuresThe proposed conduits are derived from two typesthe solid-state radical ion pairs (exTTFP+•C 60-) or of interactions,viz. sulfur-sulfurinteractionsbetween two neighboringexTTF units and the enclosed fullerenethat bridges between two porphyrints terminalfullerenes also interactwith the concave exTTF-porphyrindsowever, such interactions do not provide a more direct conduintis may explain the lack of conductivity seen upon photoexcitation. The differencesin conductivitiesbetween the two SOF systems eported here can be rationalized in terms f the better inherent conductive properties of pristine® Celative to C_{60}^{39} In addition, the closerpacking of the larger and ellipticalC₇₀ serves to push the exTTF units closer together, which is expected to lead to a more favorable loekstcron transfer and overall conductivity for ure 5c,d)To compare the effective packing within these two host-guestmbinations, Hirshfeld surfaceanalyseswere carried out. These revealed more extensive supramolecular interactions when was bound as the guest inside the pseudohexagecreptor site as compared with 6 (Figure S56a,b)t should also be noted that under conditions of reductionisCknown to form radicalanion dimers; these could serve as traps that preclude effective conductivity.

CONCLUSIONS

In summary, a new exTTF-porphyrin-based multitopic receptor has been synthesizede unique designproviding two distinctive binding sites allows for the stabilization of

hierarchicaBD solid-statesupramoleculanetworksin the presence of Gand G_0 Photophysical measurements revealed partialshort-lived (108 ps) CT transitions in solution and in (exTTFP⁺•C₇₀⁻⁻). The inference of CT interactions involving the exTTF-porphyrin 2 and the test fullerene guests led to explorationsof the presentSOFs as potential conductive materialsA significant conductivity enhancement (* fold) was observed in the case of (2) Orelative to what was seen for the pristine form of receptor 2.A 100-fold reduction in conductivity was seen for the correspondingletived SOF, which is ascribed to changes in the conductance pathway as well as geometricated electronic differences in the specific fullereneemployed. This work thus serves to highlight a convenient approach to controlling the charge mobility in selfassembled ensembles via the appropriate choicecéptor (2) and adjuvant(C_{60} or C_{70} in the presentinstance). The ability to effect control this way has important implications for the design of new organic charge-transpotevicesand could lead to the developmentof new highly conductive organic materials entirely based on nebuilding blocks.

ASSOCIATED CONTENT

Supporting Information The Supporting Information isavailablefree of chargeat https://pubs.acs.org/doi/10.1021/jacs.0c03699.

> Generalexperimentasection, synthesis and characterization, electrochemical and spectroelectrochemical data. additional photophysicaldata, TAS data, theoretical studieson 2 and its fullerene complexes Hirshfeld

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surface analyses and single-crystadonductivity experiments (PDF)

Crystallographic data for 2 (CCDC 1970803) (CIF) Crystallographic data $fo(2 \cdot C_{60})_n$ (CCDC 1991549) (CIF)

Crystallographic data fo(2•C₇₀)_n (CCDC 1991548) (CIF)

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