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Rational Design, Synthesis, and Optical Properties of Film-Forming, Near-Infrared Absorbing, and Fluorescent Chromophores with Multidonors and Large Heterocyclic Acceptors

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Abstract: A new series of film-forming. low-bandgap chromophores (1a,b and 2a,b) were rationally designed with aid of a computational study, and then synthesized and characterized. To realize absorption and emission above the 1000 nm wavelength, the molecular design focuses on lowering the LUMO level by fusing common heterocyclic units into a large conjugated core that acts an electron acceptor and increasing the charge transfer by attaching the multiple electron-donating groups at the appropriate positions of the acceptor core. The chromophores have bandgap levels of 1.27-0.71 eV, and accordingly absorb at 746-1003 nm and emit at 1035-1290 nm in solution. By

design, the relatively high molecular weight (up to 2400 gmol^{-1}) and noncoplanar structure allow these near-infrared (NIR) chromophores to be readily spin-coated as uniform thin films and doped with other organic semiconductors for potential device applications. Doping with [6,6]-phenyl-C₆₁ butyric acid methyl ester leads to a red shift in the absorption only for **1a** and **2a**. An interesting NIR electrochromism was found for **2a**, with absorption

Keywords: absorption • chromophores • films • heterocyclic receptors • near-infrared • photoluminescence being turned on at 1034 nm when electrochemically switched (at 1000 mV) from its neutral state to a radical cation state. Furthermore, a large Stokes shift (256-318 nm) is also unique for this multidonor-acceptor type of chromophore, indicating a significant structural difference between the ground state and the excited state. Photoluminescence of the film of 2a was further probed at variable temperatures and the results strongly suggest that the restriction of bond rotations certainly helps to diminish non-radiative decay and thus enhance the luminescence of these large chromophores.

Introduction

A large number of the donor–acceptor (D–A) type of conjugated organic compounds, oligomers, and polymers having bandgap energies between 1.75 and 3.1 eV are known and typically absorb or emit in the visible spectral region.^[1] The design and realization of low-bandgap organic chromophores (e.g., 1.19–0.56 eV or 800–1600 nm) are of current interest, owing to their potential applications such as fluorescent contrast agents for bio-imaging in the near-infrared (NIR) spectral region,^[2] NIR light-emitting diodes for information-secured display and background lighting,^[3] NIR photodetectors,^[4] and NIR photovoltaic devices.^[5] Besides NIR absorption and fluorescence, other stimulus-responsive properties such as NIR electrochromism have also attracted a great deal of interest for potential use in devices for modulating NIR light (e.g., at 1310 and 1550 nm).^[6]

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Among various types of NIR chromophores, much effort has been directed toward the design and synthesis of chromophores composed of powerful electron donor (D) and acceptor (A) units for use as either active components in devices or building blocks for the synthesis of oligomers and polymers with a wide range of optoelectronic properties. Andersson et al. systematically studied the D–A and D-A-D types of low bandgap polymers.^[7] Their work has clearly demonstrated that linear polymers can be designed to absorb in the visible and NIR spectral region or over the other way to further narrow the bandgap of the D–A molecular systems is to extend the π -conjugation of the known acceptors and thus to induce a more efficient intramolecular charge transfer (CT).^[9] There is a group of well-known electron-deficient heterocyclics, such as hexaazatriphenylene (HAT),^[10] benzene-fused HAT derivatives,^[11] and quinoxalino[2', 3', 9, 10]phenanthro[4,5-abc]phenazines (PPP);^[12] however, none of them are able to yield NIR-absorbing chromophores. For example, PPP-Ph and HAT-Ph

(Scheme 1) were reported to have the bandgaps of 2.78 and

solar spectrum and are promising candidates for use in single or tandem solar cells. With respect to small low-bandgap molecules, we recently reported a series of NIR photoluminescent and electroluminescent chromophores containing benzobis(thiadiazole) (BBT) as a stronger electron acceptor, rather than the commonly used benzothiadiazole (BT).^[8] As the LUMO level of these chromophores is lowered due to the presence of a strong acceptor of BBT, the absorption and emission are typically pushed into the NIR region (>800 nm).

However, any strong electronic interaction in the D-A type of conjugated molecular systems does not render them

either strong electron donors or acceptors. In practice, D and A components are often covalently linked by a conjugated spacer (D- π -A), thus favoring stronger electronic coupling and lowering the bandgap. Nevertheless, there is a realistic limitation to the availability of very strong acceptors and donors. Alternative approaches to the design of lowbandgap molecular systems are urgently needed. In this work, we intend to demonstrate another approach to lowbandgap chromophores with a low LUMO level by using a large heterocyclic acceptor with extended conjugation and as well by attaching multiple electron-donating groups at the appropriate positions of the acceptor core. Herein, we report the design, synthesis, and characterization of a new series of multi-armed disk-like D-A type of NIR chromophores having a large heterocyclic acceptor as a core. In addition, the HOMO and LUMO levels of the new chromophores (1a,b and 2a,b) and the chromophores having structurally similar but less conjugated heterocyclic cores are calculated and compared.

Results and Discussion

Design and synthesis: Considering the limited availability of the known electron-withdrawing groups as an acceptor, an-



HOMO = 6.30 eV, LUMO = 3.10 eV, E = 3.20 eV HOMO = 6.00 eV, LUMO = 3.80 eV, E = 2.20 eV

Scheme 1. Computation-aided rational design of low-bandgap chromophores with large heterocyclic cores as an acceptor with low LUMO levels.

2.85 eV, or HOMO/LUMO energies of 5.92/3.25 and 6.37/ 3.70 eV, respectively.^[12] The calculations indicate that PPP-Ph and HAT-Ph have a similar bandgap, 3.30 and 3.20 eV, respectively (Scheme 1). However, by fusing a thiadiazole unit onto PPP and HAT cores, our calculations show a large decrease in the LUMO levels (3.50 and 3.80 eV from 2.70 and 3.10 eV, respectively), resulting in a significant decrease in the bandgap for hypothetic PPP-BT (2.30 eV) and HAT-BT (2.20 eV).

Encouraged by computation-aided design, we intend to fuse some common heterocyclics together as a route to new electron acceptors. In particular, we can combine benzothiadiazole and the PPP and HAT units to form a new π -conjugated heterocyclic as an acceptor with a lower LUMO level. At the same time, the donor groups are placed in a less congested position, unlike the twisted vicinal phenyl groups in HAT-Ph, to ensure a better conjugation and thus a more efficient D-A transfer. Therefore, new chromophores would have a lower bandgap and become NIR-absorbing and fluorescent. In this work, we report a new series of multidonoracceptor type NIR chromophores having large HAT-BT and PPP-BT cores as the new acceptor (Scheme 1). The triangular HAT-BT core has extended π -conjugation and can be attached to up to six electron donors. The length of the planar, rod-like PPP-BT core is longer than that of the

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HAT-BT core, but its overall electron delocalization may be interrupted by the tetrahydropyrene resonance structure. The selection of the donors is quite flexible because many electrondonating groups are known. In addition, the donor groups are expected to impart good solubility and film-forming properties to the designed chromophores owing to their twisted and branched structures (TPA and long alkyl groups on fluorene), the large molecular size, and the relatively high molecular weights.

Scheme 2 outlines the synthetic routes to four representative chromophores (**1a,b** and **2a,b**). The starting materials (**3a,b**) were obtained by a Stille coupling reaction between 4,7dibromo-5,6-dinitro-2,1,3-benzothiadiazole and tributyltin derivatives of the corresponding donors (**a** and **b**, Scheme 2).^[8] Reduction of the nitro groups



Scheme 2. Synthesis of NIR chromophores 1a,b and 2a,b.

Table 1. Optical and electrochemical properties and bandgap data of chromophores.

	$\lambda_{\max}^{abs}[nm]^{[a]}$	$\lambda_{\max}^{abs} [nm]^{[b]}$	$\lambda_{\max}^{abs}[nm]^{[c]}$	$\lambda_{max}^{PL}[nm]^{[a]}$	Stokes shift [nm] ^[a]	HOMO/L exptl ^[d]	UMO[eV] calcd	Band $E^{[d]}$	$gap[eV E_{op}^{[e]}]$	E_{calcd}
1 a	932, 665	971, 685	1035, 713	1250	318	4.97/4.00	4.30/3.30	0.97	1.01	1.00
1 b	1003, 680	1040, 702	1054, 711	1290	287	5.15/4.44	5.00/3.90	0.71	0.97	1.10
2 a	746	772	798	1035	279	5.00/3.73	4.80/3.30	1.27	1.40	1.50
2 b	844	864	856	1100	256	5.08/3.86	5.60/3.60	1.22	1.24	2.00

[a] Measured in toluene with a concentration of 1×10^{-5} M. [b] Measured as a film. [c] Measured with PCBMdoped films (1:1 w/w). [d] From electrochemical data, $E(\text{HOMO}) = -(E_{\text{ox}} + 4.44)$ [eV], $E(\text{LUMO}) = -(E_{\text{red}} + 4.44)$ [eV]. [e] Optical bandgap (op) = $1240/\lambda_{\text{abs}}^{\text{onset}}$ [eV]

in **3a,b** was best carried out in acetic acid at 80 °C using iron powders to afford diamines **4a** and **4b** in good yields. Subsequent condensation reactions with hexaketocyclohexane and pyrene-4,5,9,10-tetraones afforded chromophores **1a,b** and **2a,b** in 40–60 % yields, respectively.

Characterization: The final products were characterized by spectroscopic means, and their structures are consistent with the spectral data (see the Supporting Information). Owing to the long alkyl groups and the twisted donor moieties relative to the core, these chromophores are quite soluble in common organic solvents such as chloroform, tetrahydrofuran, toluene, and xylene. Furthermore, owing to their high molecular weights (up to 2400 gmol^{-1}) and non-coplanar structures, the uniform thin films can be readily obtained by spin-coating. The onset temperatures for 5% weight loss in nitrogen, as assessed by thermogravimetry, are 399°C and 365°C for **1a** and **1b**, and 395°C and 388°C for **2a** and **2b**, respectively (Figure S1).

Electrochemical properties: The electrochemical properties of the chromophores were investigated by cyclic voltammetry (CV) in dichloromethane (DCM) with a concentration of 10^{-3} M (Figure S2). The chromophores are all electrochemically active and have two or three quasi-reversible oxidation and reduction waves (Table 1). The reduction occurs at the heterocyclic cores of these chromophores, while the two reversible oxidation waves of **1a** and **2a** are attributed to the oxidation of the triphenylamine (TPA) moiety.

Bandgap energy and computational study: The HOMO, LUMO, and bandgap levels of these compounds, as determined from their electrochemical data, coincide well with the values calculated from their absorption data and from theoretical calculations (Table 1). Although the HOMO levels of all the compounds are $\approx 5.00 \text{ eV}$, their LUMO levels are quite different. This difference is clearly related to the delocalization of π -electrons in the HAT-BT and PPP-BT cores. As a result, the HAT-BT series have a lower bandgap (0.71 and 0.97 eV) than the PPP-BT series (1.22 and 1.27 eV). Compound 1b has the lowest bandgap (0.71 eV) among all, which is believed to be mainly due to better conjugation and an efficient CT process between the fluorene donor and the HAT-BT acceptor via the thiophene bridging unit. In comparison, 2a has a bandgap of 1.27 eV, owing to its relatively higher LUMO (3.73 eV).

To compare the delocalizing effects, Figure 1 shows the calculated LUMOs of the reference compounds along with the novel compounds. The structures and orbitals in these drawings were rendered using the same scale and isovalues (0.01 a.u) to allow a visual comparison of the MOs. When comparing PPP-BT vs. PPP-Ph, it is clear that the benzo-thiadiazole moiety of the former compound gives an additional delocalization advantage. Furthermore, steric interference between the two neighboring phenyl groups in PPP-Ph forces mutual twisting, which diminishes conjugation to the central unit. In PPP-BT, however, the phenyl group is less twisted relative to the core. Accordingly, this design feature allows better delocalization or more efficient charge trans-

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Figure 1. Comparison of LUMO spatial distribution (isovalue = 0.01 a.u.).

fer, as evidenced by extended delocalization to the electrondonating moieties of **2a** and **2b**, in particular even to the fluorene moiety of **2b**. A comparison of the hexaazatriphenylene series shows again that steric interference of vicinal phenyl groups in HAT-Ph does not allow perfect delocalization. The delocalization in compounds **1a** and **1b** extends further into the side chains, creating large chromophores with the smallest bandgaps (Table 1).

Absorption and photoluminescence in solution: The absorption and photoluminescence of all chromophores were recorded in toluene (Figure 2). The absorption bands in the UV/Vis region below 525 nm are attributed to π - π * and n- π * transitions of the conjugated aromatic segments (Table 1). The absorption bands above 600 nm are attributed to intramolecular CT transitions between the donor groups and the central acceptor cores of these chromophores. The CT bands (932 and 1003 nm) of **1 a,b** appear at longer wavelengths than those of **2 a,b** (746 and 844 nm), further indicat-



Figure 2. Normalized absorption and PL spectra of 1a,b (top) and 2a,b (bottom) in toluene $(10^{-5}m)$.

ing a greater electron-accepting ability of the HAT-BT core in **1a,b** than the PPP-BT core in **2a,b**. The absorption at relatively short wavelengths for **2a,b** could be related to the less well-delocalized PPP-BT core due to the resonance structure of tetrahydropyrene. There are two low-energy bands observed for the HAT-BT based chromophores **1a,b** (Figure 2). On changing the donor from TPA to the thiophene-bridged fluorene (**1a** vs **1b**), only the band at the longest wavelength showed a significant red shift (Δ 71 nm), while the absorption at 665 nm for **1a** was only slightly redshifted in **1b** (680 nm). Thus, the bands at 665 and 680 nm for **1a,b** seem to arise from the same or a quite similar CT transition between the HAT-BT core and an electron-donating moiety, although the exact structural origin could not be unambiguously assigned.

The NIR electrochromic properties of these chromophores were further investigated using an OTTLE cell with a concentration of 10^{-5} M in DCM containing $0.1 \text{ M Bu}_4\text{NPF}_6$. Noticeably, compound **2a** is NIR-electrochromic because a new absorption appears at 1034 nm when being electrochemically switched (at 1.0 and 1.5 V) from its neutral state to the radical cation state (Figure S3). This "turn-on" NIR absorption is probably attributable to the mixed-valence state or charge transfer within the TPA-phenylene-TPA moiety, in which one of the nitrogen centers of TPA is oxi-

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dized. On further oxidation at a higher potential (e.g., 2.5 V), the bandgap peak at 750 nm and the NIR peak at 1034 nm almost disappeared (Figure S3).

The photoluminescence of these chromophores in toluene are all above 1000 nm and vary according to their bandgap energies (Figure 2). Chromophores **1a** and **1b** emit at 1250 and 1290 nm on excitation at 932 and 900 nm, respectively. Compounds **2a** and **2b** also emit above 1000 nm (1035 and 1100 nm) on excitation at 746 and 844 nm, respectively. Fluorescence quantum yields (Φ) of these chromophores in toluene were measured relative to IR-125 (Φ =0.13 in DMSO) and found to be lower (0.83–1.97%, see the Supporting Information) than those of the D- π -A- π -D type of NIR chromophores we previously prepared.^[8]

It is interesting to note that the identical PL spectra with a maximum peak at 1250 nm were obtained for **1a**, regardless of whether excitation was at 665, 694, or 932 nm. A very large Stokes shift (256–318 nm) was also observed for these chromophores, indicating a significant structural difference between the ground state and the excited state. The large Stokes shift observed for these new NIR chromophores implies a potential application in bio-imaging because the large separation of absorption and NIR emission maxima of NIR dyes would result in a far greater signal-to-noise ratio in biomolecular imaging and would allow greater depth penetration in tissues.

The absorption and emission spectra of the four compounds were also recorded at concentrations varying from 10^{-6} to 10^{-4} mol/L. They did not show any changes in the peak positions (e.g., for **2a** in Figure S4). The results indicate that these chromophores, despite having a large π -conjugated flat core, do not readily form excimers or strong intermolecular CT in solution and have a rather weak dipole effect.

Photoluminescence in solid films: The optical properties of these chromophores were further characterized in solid films. The films were spin-coated onto a glass substrate from a chlorobenzene solution (concentration 10 mgmL^{-1}) at a speed of 1000 rpm. Typically, a 20-30 nm bathochromic shift in absorption was observed for the films compared to those in toluene (Table 1). Considering the potential photovoltaic applications of these chromophores, the films doped with [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) (1:1 by weight) were also studied. The chromophores containing the TPA donor showed a noticeable red-shift in absorption: 64 nm for **1a** and 26 nm for **2a** (Table 1 and Figure 3(top)). This red shift can be attributed to intermolecular interactions between PCBM and the TPA moieties. Because the calculation also indicates that delocalization extends more to the fluorene donor than to the TPA donors, the TPA donor is more available for intermolecular CT with the dopant. As expected, the films of 2a with or without the PCBM dopant (Figure 3(top)) show nearly the same PL spectra.

As anticipated from their chemical structures, the DSC study indicates that none of these chromophore compounds



Figure 3. Normalized absorption and PL spectra of 2a in toluene (10^{-5} M), in a film and in a film doped with PCBM (1:1 by weight) (top). Variable-temperature PL spectra of the as-prepared film of 2a (from 77.2 to 487.2 K at a heating rate of 2° Cmin⁻¹) (bottom).

has a crystalline nature. Only compound 2a shows one nonreversible solid-to-solid transition at 385 K during the first DSC heating scan up to 523 K (Figure S5) and no other transitions during the subsequent cooling and the second heating-cooling process, which implies packing or ordering in the original as-prepared solids due to its fairly large twisted structure (TPA groups relative to the planar PPP-BT core). Because the twisted intramolecular charge transfer may greatly affect the emission properties, the photoluminescence of the 2a film was further probed at variable temperatures. The PL measurement of the as-prepared spincoated film was carried out from 77.2 to 487.2 K (Figure 3 (bottom)), and the PL intensity was found to steadily decrease at a rate of 0.12 % K⁻¹ (see the Supporting Information) as the temperature rose from 77.2 to 407.2 K. However, when the solid-to-solid transition temperature of 417.2 K was reached, the PL intensity suddenly increased nearly two-fold and then continued to decrease at the same rate of 0.12% K⁻¹ (Figure 3(bottom) on the right). After cooling rapidly at the end of the first heating process, the PL intensity was about twice that of the as-prepared sample at 77.2 K (Figure S6). During subsequent heating from 77.2 to 427.2 K, the PL intensity decreased twice as fast compared to the first heating process at the rate of $0.24\% \text{ K}^{-1}$ (Figure S6). Although the exact packing or ordering of these large molecules in the solid state is unclear, the variable-temperature PL results suggest strongly that the solid-state morphology can play an important role in the PL properties of these large chromophores.

Conclusions

In conclusion, a new series of NIR-absorbing and NIR-fluorescent chromophores have been successfully designed and synthesized. The computer-aided molecular design focused on lowering the LUMO level of the acceptor by the use of a large heterocyclic with extended conjugation and by an increase in the donor-acceptor charge transfer by attaching multiple electron-donating groups at the appropriate positions of the acceptor core. Computer models were used to calculate the energies and spatial delocalization of the frontier molecular orbitals to aid and support the rational design. Theoretical and experimental data confirm that the small bandgaps of these chromophores are mainly attributed to the low LUMO levels of the acceptors and efficient multidonor-acceptor charge transfer. The NIR-absorbing and fluorescent properties, along with a very large Stokes shift and film-forming ability, make this type of chromophore potentially useful for applications in NIR photovoltaics, lightemitting diodes and bio-imaging. Our ongoing work with these new materials is focused on further in-depth studies of NIR photovoltaic devices.

Experimental Section

Computational method: The structures were drawn with MOE 2007.^[13] The geometries were initially optimized using the AM1 method in the gas phase, followed by gas-phase B3LYP/6-31G+(d) optimization using Gaussian $03^{[15]}$ running on HPCVL supercomputers.^[16] The optimized geometries were checked for negative vibrations. The HOMO and LUMO energies and coordinates were taken from the Gaussian output and the graphical orbital plots were generated with GABEDIT2.18.^[17] The calculation time was reduced by replacing the long alkyl chains of **1a** and **1b** with a methyl group.

Materials and general methods: All the chemicals and reagents were used as received from commercial sources without purification. The solvents for chemical reactions were carefully dried and purified under a nitrogen flow. All the reactions were carried out in an argon atmosphere in flame-dried glassware. Syringes were used to transfer anhydrous solvents or reagents and were purged with argon prior to use. The [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) was obtained from FEM Technology Co. 4,7-Diaryl-5,6-dinitro-2,1,3-benzothiadiazoles (**3a,b**),^[8] hexaketo-cyclohexane,^[18] and pyrene-4,5,9,10-tetraones^[19] were prepared according to the procedures reported in the literature. Details and purification methods used for **4a** and **4b** are given in the Supporting Information.

Synthesis of chromophore 1a: Hexaketocyclohexane (0.312g, 1.0mmol), 4a (4.660g, 4.0mmol), and AcOH (50mL) were added to a 250mL, round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was heated at reflux for 48h under an argon atmosphere. Column chromatography (DCM/PE 1:1 v/v) gave the pure product as a dark-green powder (1.423g, 40%). ¹H NMR (300 MHz, CDCl₃): δ = 8.00 (d, 12H, *J*=8.34 Hz), 7.15–7.00 (br, 24H), 6.71 (d, 36H, *J*=8.55 Hz); 3.82–3.80 (m, 24 H), 1.74 (m, 24 H), 1.56 (m, 24 H), 1.40–1.20 (m, 96 H), 0.88 ppm (t, 24 H, J=7.20 Hz); ¹³C NMR (100 MHz, 100 °C, C₂D₂Cl₄): δ = 157.72, 155.86, 150.62, 144.72, 142.09, 139.97, 136.44, 131.21, 128.98, 128.59, 120.23, 117.51, 117.18, 70.38, 33.24, 31.01, 30.81, 30.60, 27.60, 23.99, 15.30 ppm; IR: $\tilde{\nu}$ =3039, 2922, 2852, 1594, 1505, 1468, 1448, 1377, 1318, 1281, 1238, 1194, 1153, 1107, 1029, 978, 918, 825, 721, 697, 605, 538 cm⁻¹; elemental analysis calcd for C₂₂₈H₂₇₆N₁₈O₁₂S₃: C 76.99, H 7.82, N 7.09; found: C 77.05, H 7.99, N 7.10.

Synthesis of chromophore 1b: This was synthesized according to the procedure used to prepare 1a. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether 1:4 v/v) to afford the product as a dark-green solid (40%). ¹H NMR (400 MHz, 100°C, $C_2D_2Cl_4$): $\delta = 9.23$ (s, 6H), 8.61 (s, 12H), 8.46 (s, 6H), 8.41-8.30 (br, 36H), 2.00 (s, 24H), 1.15-0.98 (br, 144H), 0.78 (d, 36H) ppm; ¹³C NMR (100 MHz, 100 °C, $C_2D_2Cl_4$): $\delta = 154.29$, 153.74, 153.19, 152.81, 145.24, 142.71, 142.25, 139.44, 138.61, 137.97, 134.96, 128.56, 128.30, 126.91, 126.07, 124.66, 124.07, 121.97, 121.49, 121.29, 56.74, 41.76, 33.17, 31.48, 30.63, 25.54, 23.92, 15.28 ppm; IR: v=3061, 2924, 2851, 1605, 1522, 1502, 1465, 1407, 1377, 1268, 1240, 1175, 1134, 1100, 1065, 1005, 915, 825, 802, 778, 737, 630, 538, 443 cm⁻¹; elemental analysis calcd for C₂₂₂H₂₅₈N₁₂S₉: C 78.81, H 7.69, N 4.97; found: C 78.90, H 7.79, N 5.15. Synthesis of chromophore 2a: Pyrene-4,5,9,10-tetraones (0.262 g, 1.0 mmol), 4a (2.680 g, 2.3 mmol), and AcOH (50 mL) were added to a 250 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was heated at reflux for 48 h; it was initially orange in color, then turned red. After 12 h, the color was still red and there was some solids in the flask. Column chromatography (DCM/PE=1:1 v/v) gave the pure products as a dark-green powder (1.523 g, 60 %). ¹H NMR (300 MHz, CDCl₃): $\delta = 9.26$ (d, 4H, J = 7.77 Hz), 8.01 (d, 8H, J =8.67 Hz), 7.95 (t, 2H, J=7.89 Hz); 7.28 (d, 16H, J=9.00 Hz), 7.21 (d, 8H, J=7.92 Hz), 6.92 (d, 16H, J=6.27 Hz), 3.97 (t, 16H, J=6.45 Hz), 1.79 (m,16H), 1.44 (m, 16H), 1.34-1.30 (m, 64H), 0.87 ppm (t, 24H, J= 6.60 Hz); ¹³C NMR (100 MHz, 100 °C, $C_2D_2Cl_4$): $\delta = 157.80$, 154.76, $150.70,\ 144.65,\ 142.35,\ 139.31,\ 135.77,\ 132.05,\ 130.73,\ 130.63,\ 130.53,$ 128.79, 120.28, 117.64, 70.49, 33.23, 31.03, 30.81, 30.60, 27.61, 23.98, 15.30 ppm; IR: $\tilde{v} = 3039$, 2924, 2854, 1597, 1505, 1457, 1419, 1365, 1319, 1262, 1238, 1194, 1166, 1145, 1110, 1029, 990, 910, 866, 827, 810, 722, 699, 645, 624, 605, 586, 539, 527, 499, 448, 411 cm⁻¹; elemental analysis calcd for $C_{164}H_{190}N_{12}O_8S_2$: C 78.12, H 7.60, N 6.67; found: C 77.94, H 7.71, N 6.77.

Synthesis of chromophore 2b: This was synthesized according to the procedure used to prepare **2a**. The crude product was purified by column chromatography (silica gel, dichloromethane: petroleum ether 1:4 v/v) to afford the product as a brown powder (40%). ¹H NMR (400 MHz, 100°C, $C_2D_2Cl_4$): δ =9.83 (d, 2H, *J*=6.00 Hz), 9.07 (s, 4H), 8.24 (t, 2H, *J*=7.2 Hz), 7.85 (s, 8H), 7.77-7.70 (m, 8H), 7.54 (s, 4H), 7.38 (s, 4H), 7.33 (s, 8H), 2.14 (s,16H), 1.16-1.14 (br, 96H), 0.77 (s, 24H) ppm; ¹³C NMR (100 MHz, 100°C, $C_2D_2Cl_4$): δ =153.43, 153.29, 152.80, 151.76, 144.23, 142.85, 142.26, 138.04, 137.62, 136.92, 134.95, 131.61, 128.68, 128.43, 126.66, 124.74, 122.43, 121.79, 121.65, 121.39, 56.86, 41.82, 33.19, 31.70, 30.74, 30.61, 25.71, 13.93, 15.26 ppm; IR: $\bar{\nu}$ =3064, 2954, 2924, 2851, 1605, 1518, 1491, 1456, 1420, 1375, 1329, 1308, 1260, 1210, 1154, 1066, 1020, 912, 877, 800, 776, 735, 715, 576, 536, 497, 442 cm⁻¹; elemental analysis calcd for C₁₆₀H₁₇₈N₈S₆: C 79.89, H 7.46, N 4.66; found: C 79.94, H 7.73, N 4.63.

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