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# Article

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# Photoswitchable J-aggregated Processable Organogel by Integrating a Photochromic Acceptor

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Abstract: A novel  $\pi$ -chromophoric 1,4-bis(anthracenylethynyl)benzene (BAB) based highly emissive J-aggregated organogel has been synthesized and characterized. Single crystal structure determination of asymmetric  $\pi$  chromophoric bola-amphiphilic **BAB1** (dodecyl and triethyleneglycolmonomethylether (TEG) containing side chains of bis(anthracenylethynyl)benzene) supports J-aggregation. Further, a photochromic acceptor chromophore 4,4'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carbaldehyde) (**PBMC**) is non-covalently encapsulated in the gel and photoswitching studies have been performed based on pcFRET. The modulated emission of the processable soft material is further exploited for rewritable display. However, **BAB2** (dodecyl side chain on both sides) does not show gelation property due to its low solubility.

# Introduction

 Reversible modulation of emission intensity of a fluorescent system has attracted significant attention because of its potential application in several areas such as optical data storage,<sup>1</sup> sensing,<sup>2</sup> and fluorescence microscopy<sup>3</sup>. Such intriguing class of compounds can be prepared by covalent/non-covalent integration of organic fluorophores with a suitable photochromic molecule.<sup>4</sup> The fluorescence modulation relies on the photochromic Förster resonance energy transfer (pcFRET)<sup>4,5</sup> process and photoinduced charge/electron transfer (PET)<sup>6</sup> where fluorescence of the donor is quenched by the wavelength selective photoirradiation of an acceptor photochrome. Among the different photochromic molecules, di(thiophenyl)ethene (DTE) are widely used because of their reversible photo-conversion between a colorless open to a colored closed form, ease of functionalization, high chemical/thermal stability and fatigue resistance.<sup>7</sup> DTE has been hybridized in several chromophoric system for pcFRET such as BODIPY, anthracene, oligothiophene, perylene, porphyrin, rhodamine, metal complexes and semiconductor quantum dots.<sup>8</sup>

Scheme 1. Schematic Showing Photo-switching Gel Material Based on pcFRET.



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With the aim of developing a new pcFRET system, we have utilized a J-aggregated fluorophoric material as an efficient FRET donor. The J-aggregated fluorescent systems render several advantages, which accounts for their wide applicability, including narrow red-shifted emission, high quantum efficiency/brightness in aggregated state, extreme stability and long-lived excited state lifetime.<sup>9</sup> However, design and synthesis of J-aggregated fluorophore is a highly challenging assignment as most fluorophores undergo H-aggregation resulting in aggregation induced emission quenching.<sup>10</sup> Furthermore, the gel state will provide additional advantages of easy processability as well as proper alignment of acceptor fluorophores for efficient FRET process.<sup>11,12</sup>

Herein, we report the design and synthesis of a novel  $\pi$ -chromophoric asymmetric bola-amphiphilic 1,4-bis(anthracenylethynyl)benzene (BAB1) based J-aggregated emissive gel BAB1-G (Scheme 1). The central phenyl ring of BAB1 was strategically decorated with mixed side chain functionality n-dodecyl (non-polar) polar i.e. a and triethyleneglycolmonomethylether (TEG, polar) to induce gelation as well as solubility. The side chain functionalities directed to a parallel offset packing ( $\theta_1 = 46.1^\circ \& \theta_2 = 50.0^\circ$ ) of the  $\pi$  chromophores resulting in the J-aggregation. Further, a photochromic acceptor molecule DTE has been noncovalently encapsulated to study photoswitching property based on pcFRET. The ensemble demonstrated photoinduced ON-OFF energy transfer and utilized for rewritable display. In contrast, synthesized **BAB2** (Scheme 2a), which contains dodecyl chains on both sides did not show any gelation property due to its low solubility in common organic solvents indicating the necessity of mixed polar side chain functionality to induce solubility and corresponding gelation (Table S1).

## **Results and Discussion**

The designed BAB derivatives, **BAB1&2** were synthesized by Pd(0) catalyzed Sonogashira-Hagihara cross-coupling reaction between 9-ethynylanthracene and functionalized 1,4diiodobenzene in 2:1 stoichiometry (Scheme S1&2, SI).<sup>13</sup> The DTE derivative, 4,4'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carbaldehyde) (**PBMC-open**) was synthesized by following a reported procedure (Scheme S3, SI).<sup>14</sup> The UV-Vis spectrum of a methanolic solution ( $10^{-6}$  M) of **BAB1** shows two vibronic absorption bands at 440 and 460 nm (molar extinction coefficient =  $2.1 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>), and the solution exhibits cyan emission with two overlapping bands at 479 and 505 nm when excited at 460 nm (Figure 1a,b). The Stokes shift is around 19 nm. **BAB2** also displayed UV-Vis (molar extinction coefficient =  $2.2 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>) and PL spectra (Figure S1) similar to **BAB1** due to structural similarities. Strikingly, in solid state, both **BAB1&2** exhibited a new red-shifted absorption band at 509 and 501 nm, respectively (Figure 1a/S1a). The corresponding excitation resulted in bright-red emission with maximum at 617 nm and 591 nm for **BAB1** and **BAB2**, respectively (Figure1b/S1b). The mirror-image relationship of UV-Vis and PL spectra in

Scheme 2. (a) Structures of **BAB1&2** With Their Photograph in Solid State and Methanolic Solution Under UV Light. (b) Open and Closed Form of **PBMC** Along With Photographs in Methanolic Solution.



solution, appearance of a distinct red-shifted absorption band and bright-red emission (Scheme 2a) in the solid state intrigued us to investigate the aggregation behavior. For this, UV-Vis and PL measurements were carried out with methanolic solutions by successive

addition of water as "poor solvent" which triggers intermolecular aggregation (Figure 1c,d/S2).<sup>15</sup> Notably, the water addition with **BAB1** solution resulted in a new absorption band at 505 nm. This band can be attributed to J-aggregation due to it's red-shifted appearance.<sup>9</sup> The aggregation also resulted in an additional red-shifted emission band at 570 nm ( $\lambda_{exc} = 505$  nm). Dynamic light scattering (DLS) revealed that the aggregated particles have hydrodynamic radius centered at 817 nm (Figure S3). Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) also showed the presence of aggregated particles (Figure S4, S5). However, the aggregation-based emission band predominates in the solid at 617 nm (Figure 1b). The emission quantum yield of **BAB1** in methanol is 36%. The emission property remains similar in solid state as the observed quantum yield is 27%. The fluorescence lifetime was found to be 2.28 and 2.51 ns in solid and methanolic solution, respectively. All these observations clearly supported the J-aggregation behavior of **BAB1**. **BAB2** also revealed the appearance of J band upon successive addition of water in methanolic solution (Figure S2).



Figure 1. (a) UV-Vis and (b) PL spectra of **BAB1** in methanol (10<sup>-6</sup> M,  $\lambda_{exc} = 460$  nm), methanol/water (1:1,  $\lambda_{exc} = 505$  nm), xerogel ( $\lambda_{exc} = 509$  nm) and solid ( $\lambda_{exc} = 509$  nm).

Volume corrected UV-Vis (c) and emission spectra (d) of a methanolic solution of **BAB1** (10<sup>-6</sup> M) with varied amount of water. Volume correction to the absorbance was performed by multiplying absorbance with  $\{(V+x)/V\}$ , where V = initial volume and x = volume of added water. (e) Thermo reversibility test of **BAB1-G** (14.6 mM). (f) Digital photograph of **BAB1-G** (14.6 mM) under UV light and (g) TEM image of **BAB1** xerogel.

**BAB1** forms a gel **BAB1-G** in a mixture of 5:1 methanol:dichloromethane, instantaneously (Figure 1e,f).<sup>16</sup> The formation of gel was confirmed by inversion test. Sol-gel thermo reversibility of the gel was also observed. The preformed gel was converted to a sol phase upon heating at 60 °C and the produced sol was transformed again into a gel phase by cooling to room temperature. Moreover, the gel also formed sol phase upon sonication and again returned to a gel phase upon standing. This indicated thixotropic nature of the gel. The critical gelation concentration of **BAB1** was found to be 12.1 mM. FESEM and TEM microscopy demonstrated a cross-linked fibrous network of **BAB1** xerogel (Figure 1g/S6/S7). **BAB1** also exhibited high emission in the gel phase with 34% fluorescence quantum yield (Figure 1f). The UV-Vis spectrum of **BAB1** xerogel showed two vibronic absorption bands at 470 and 446 nm, and a J-band at 509 nm (Figure 1a). Excitations at these wavelengths resulted in a broad emission in the range of 530-700 nm with a maximum at 608 nm (Figure 1b).



Figure 2. Parallel offset arrangement of BAB1. Distances are given in angstrom unit (Å).

Further to support and understand the molecular packing leading to J-aggregation, **BAB1** was successfully crystallized by slow evaporation technique from a solution of toluene at room temperature. Red colored rhombus shaped single crystals of **BAB1** were obtained and single crystal X-ray diffraction (SXRD) revealed that **BAB1** crystallized in the triclinic  $P\overline{1}$ space group wherein each molecule consists of a rigid core formed by two terminal anthracenyl moieties and one central phenyl ring, connected by two ethynyl modules (Figure 2, S8-12, Table S2). All these aromatic moieties are coplanar. The individual molecules of **BAB1** are packed in parallel offset fashion via multiple C-H $\cdots\pi$  interactions between hydrogens of dodecyloxy chain and  $\pi$  cloud of the anthracenyl group from adjacent molecule. The C–H $\cdots\pi$  distances are in the rage of 2.756 – 3.036 Å. Time-dependent density functional theory (TD-DFT) computation on a model system of BAB1 revealed that the direction of transition electric dipole moment (TEDM) of the longest wavelength electronic transition (HOMO $\rightarrow$ LUMO,  $\lambda = 534$  nm, f = 1.19) is parallel to the long axis of molecule i.e. parallel to the conjugated backbone (see SI). Along this direction, the offset in crystal packing ( $\theta_1$  = 46.1° &  $\theta_2 = 50.0^\circ$ , Figure 2) remains in the range of J-aggregation (J-aggregate:  $0^\circ < \theta < 54.7^\circ$ ; H-aggregate: 54.7°< $\theta$ <90°).<sup>17</sup> The simulated PXRD pattern displayed a peak at  $2\theta = 24.2^{\circ}$ 

(222) which passes in between two molecules and parallel to the  $\pi$  conjugated backbones (Figure S12). The peak is retained in solid, methanol/water (1:1) aggregates and xerogel of **BAB1**, indicating similar  $\pi$  arrangement between the chromophoric backbone of **BAB1**(Figure S13). Notably, **BAB2**, in solid state, also displayed the peak at  $2\theta = 24.2^{\circ}$ , thus showing presence of similar  $\pi$  arrangement as of **BAB1** and combination of UV-Vis studies (*vide supra*) supported J aggregation in **BAB2**(Figure S14).

Since, the central phenyl ring of **BAB1** contains both hydrophilic (TEG) and hydrophobic (n-dodecyl) side chains, we measured water contact angle on a gel coated glass surface to understand exterior decoration. The measured contact angle was 44°, indicating exterior decorated TEG chains and, consequently, n-dodecyl chains pointed inward direction of the film (Figure S15). Since the gelation was performed in methanol medium (major), TEG groups got exposed on the outer surface of the film in order to reduce surface energy.

**PBMC** was chosen to incorporate in the gel to study ON-OFF energy transfer process via pcFRET as it can be switched between open (**PBMC-open**) and closed form (**PBMC-closed**) by UV (365 nm) and visible light (590 nm) irradiation, respectively (Scheme 2b). Moreover, **PBMC-closed** exhibited an absorption band in the range 490-730 nm with a maximum at 622 nm (purple color) which has partial overlap with the emission band of **BAB1-G** (500-700 nm) (Figure 3a). This overlap is desirable for excitation energy transfer from **BAB1** to **PBMC**. The open form showed no absorption in the emission range of **BAB1-G**, indicating that **PBMC-open** cannot act as an acceptor of the emitted energy from **BAB1-G**. The formyl substitutions in **PBMC** results in red-shifted absorption spectrum and facilitates faster kinetics of interconversion between open and closed form allowing to study ON-OFF energy transfer process.<sup>18</sup> Moreover, **PBMC** can be embedded easily into the gel matrix by multiple supramolecular interactions such as  $C-H\cdots\pi$ ,  $C-F\cdotsH$ ,  $\pi$ -stacking etc.

Therefore, **PBMC** incorporated gel would be suitable to study photo modulated emission via ON-OFF energy transfer process.



Figure 3. (a) UV-Vis spectra of **PBMC-open** and **PBMC-closed**, and emission spectrum of **BAB1-G** ( $\lambda_{exc} = 470 \text{ nm}$ ). (b) ON-OFF energy transfer study of **PBMC@BAB1-G** (14.6 mM) by emission spectroscopy ( $\lambda_{exc} = 470 \text{ nm}$ ) in gel phase. (c) Digital photograph of gel coated glass slide (under UV light) before and after masked UV irradiation (JNC), (d) ON-OFF energy transfer cycles, (e) UV-Vis spectra with digital photographs and (f) fluorescence lifetime of **PBMC@BAB1-G** before and after 25 min UV light irradiation (365 nm).

Incorporation of **PBMC-open** (30 mol%) in **BAB1-G** was performed in situ during gel formation to obtain **PBMC-open@BAB1-G**. Upon **PBMC-open** incorporation, the J band in UV-Vis spectrum was blue shifted by 8 nm (509 nm $\rightarrow$ 501 nm) and the emission band was red-shifted by 6 nm (578 nm $\rightarrow$ 584 nm). Elemental mapping by Energy-Dispersive X-Ray Spectroscopy (EDS) revealed homogeneous distribution of **PBMC** into the gel phase (Figure S16). The PXRD of **PBMC@BAB1-G** showed moderate crystallinity with shift in several peak positions when compared with **BAB1-G**, indicating change in packing upon

**PBMC** encapsulation (Figure S17). Importantly, the PXRD pattern showed retention of the peak at  $2\theta = 24.2^{\circ}$  ((22 $\overline{2}$ ) plane) after encapsulation of **PBMC-open**, indicating retention  $\pi$ arrangement and J aggregation. Notably, the emission intensity of **BAB1-G** was retained upon **PBMC-open** incorporation as the quantum yield was measured to be 30%. The ON-OFF energy transfer process was studied by PL spectroscopy, excited state fluorescence lifetime and quantum yield measurement (Figure 3). For this study, PBMC-open@BAB1-G was irradiated with 365 nm light (intensity: 308  $W/m^2$ ) for 25 min. The irradiation resulted in greenish-orange color of the gel (Figure 3e, inset) and the UV-Vis spectrum showed appearance of 622 nm band, indicating the formation of PBMC-closed@BAB1-G (Figure 3e). Interestingly, the emission intensity ( $\lambda_{exc} = 584$  nm) was quenched by ~80% and the fluorescence lifetime was decreased to 360 ps from 2.36 ns (Figure 3b,d,f). The quantum yield was drastically reduced to 2.5% upon UV irradiation. In the next step, visible light irradiation ( $\lambda = 590$  nm, intensity = 796 W/m<sup>2</sup>) on **PBMC-closed@BAB1-G** for 2 h, converted **PBMC-closed** to **PBMC-open** as evident from the disappearance of 622 nm band in UV-Vis spectrum and, consequently, the emission intensity regenerated completely. These observations are strongly supportive of the occurrence of energy transfer from **BAB1** to **PBMC** in its closed state and absence of such process in the open form. Notably, incorporation of 35 mol% PBMC into BAB1-G resulted in complete energy transfer process as observed by the complete emission quench upon UV irradiation (Figure S18). However, the result demonstrated an on-demand energy transfer process in a highly processable material. The material was coated on a glass slide and rewritable capability was demonstrated by masked UV irradiation (Figure 3c). The ON-OFF energy transfer assisted reversible emission quench and regain was verified up to three cycles (Figure 3d). The rate constants for fluorescence decay and enhancement, due to light induced ring opening and closing reactions of **PBMC** in gel phase, were calculated by fitting the relative change in emission intensity at 584 nm with mono-exponential function (Figure S19). The fluorescence decay and

enhancement profile revealed a rate constant of  $2.08 \times 10^{-3}$  s<sup>-1</sup> and  $2.05 \times 10^{-4}$  s<sup>-1</sup>, respectively. Free energy calculations based on DFT, at B3LYP/6-31G\* level, indicated that the electron transfer processes from the photoexcited **BAB1** (**BAB1\***), **PBMC-open** (**PBMC-open\***) and **PBMC-closed** (**PBMC-closed\***) to the counter component in ground state are thermodynamically unfavorable (see SI). Therefore, an alternative PET mechanism is not considered.

## Conclusions

The forgoing results demonstrate development of a highly processable soft material with tunable optical property via ON-OFF energy transfer process. **BAB1** displayed high quantum yield 28-36% ranging from gel to solid phase due to J-aggregation. The adopted functionalization strategy allowed parallel offset packing leading to J-aggregation via multiple  $C-H\cdots\pi$  interactions between dodecyl side chain and anthracene moiety as evident from the crystal structure. The mixed-polar side chain functionality in **BAB1** resulted in gelation allowing facile encapsulation of **PBMC** into the gel matrix for successful ON-OFF energy transfer via pcFRET. This finding could potentially broaden the landscape of J-aggregated emission as a donor for photo-switchable optoelectronic applications.

#### **Experimental Section.**

**General.** All commercially available solvents and reagents were purchased and used without further purification.  $Pd(PPh_3)_4$ , hydroquinone, 1-bromododecane, 2-(2-(2methoxyethoxy)ethoxy)ethanol, iodine monochloride, 18-crown-6, *p*-toluene sulfonyl chloride, 9-bromoanthracene, and trimethylsilyl acetylene were purchased from Sigma-Aldrich chemical Co. All solvents were purchased from Spectrochem, India. 9-Ethynylanthracene,<sup>19</sup> 1-(dodecyloxy)-2,5-diiodo-4-(2-(2-(2methoxyethoxy)ethoxy)benzene,<sup>12a</sup> 1,4-bis(dodecyloxy)-2,5-diiodobenzene<sup>20</sup> and 4,4'-

(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carbaldehyde) (**PBMC-open**)<sup>21</sup> were synthesized using reported procedure.

Physical Measurements. Elemental analysis was performed using a Thermo Fischer Flash 2000 Elemental Analyzer. FT-IR spectroscopy were performed on a Bruker IFS 66v/S spectrophotometer using KBr pellets in the region 4000–400 cm<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were measured utilizing a Bruker D8 Discover instrument using Cu-Ka radiation. The field emission scanning electron microscopic (FESEM) images and elemental mapping were recorded on a Nova Nanosem 600 FEI. The **BAB1** xerogels were dispersed in hexane and then drop casted onto a small piece of silicon wafer for FESEM measurements. In case of methanol/water (1:1) aggregate of **BAB1**, a 10<sup>-6</sup> M methanolic solution was treated with equal volume of water, and the resulted solution was drop casted onto a silicon wafer. For PBMC-open@BAB1, xerogel was dispersed in water and drop casted on a silicon wafer for elemental mapping via Energy-Dispersive X-Ray Spectroscopy (EDS). We chose water for dispersion as no component is soluble in water. Transmission electron microscope was measure on a JEOL JEM3010 instrument with 200 kV incident beam. The TEM samples were prepared in a similar procedure as mentioned above, but drop casted onto a carbon-coated TEM grid. BAB1 xerogel was dispersed in hexane and spin coated on a glass slide which was utilized for water contact angle measurement. The solid, gel and solution phase fluorescence quantum yield was determined by using integrating sphere, an absolute quantum yield measurement and calculated by Horiba Jobin Yvon. The synthesized gel in a cuvette was directly used for this measurement. Dynamic Light Scattering (DLS) was measured utilizing a NanoZS (Malvern UK) employing a 505 nm laser at a back-scattering angle of 173°. HR-MS was measured using Agilent Technologies 6538 UHD Accurate-Mass Q-TOFLC/MS. Perkin Elmer Lambda 900 UV-VIS-NIR Spectrometer was used for UV-Vis measurement. Perkin-Elmer model LS 55 luminescence spectrometer was utilized for PL measurement. A time-

 correlated single photon counting spectrometer of Horiba-Jobin Yvon with 350-450 nm
 picosecond Ti-saphhire laser was used for Fluorescence decay measurements. All<sup>1</sup>H spectra
 were recorded at frequency of 400 MHz using a Bruker AVANCE 400 MHz spectrometer.
 Whereas, <sup>13</sup>C-spectrum for BAB1 was recorded at 150 MHz frequency using Varian Inova
 600 MHz spectrometer.

Synthesis procedure of 9.9'-((2-(dodecyloxy)-5-(2-(2-(2-methoxy)ethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dianthracene (BAB1). A Schlenk tube was charged with 1-(dodecyloxy)-2,5-diiodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (500 mg, 739 µmol),<sup>12a</sup> 9-ethynylanthracene (374 mg, 1.85 mmol), tetrahydrofuran (20 mL) and triethylamine (2 mL). The resulting solution was degassed thoroughly with argon by freezepump-thaw method and then Pd(PPh<sub>3</sub>)<sub>4</sub> (171 mg, 148 µmol) was added to the solution. The reaction vessel was further degassed by the above-mentioned procedure. The thus degassed reaction mixture was refluxed for 36 h at 70 °C in oil-bath to complete coupling process. Upon cooling the reaction mixture to room temperature, red colored precipitate of **BAB1** was formed. The precipitate was filtered by Whatman 40 filter paper, washed with methanol and dried under vacuum to obtain **BAB1** (482mg, 79%) as pure compound. FT-IR (KBr pellet, 4000-400 cm<sup>-1</sup>): 3083 (w), 3051 (m), 2917 (s), 2848 (s), 2191 (w), 1502 (s), 1468 (s), 1427 (s), 1388 (m), 1347 (m), 1282 (m), 1219 (s), 1202 (s), 1120 (s), 730 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.87$  (t, J = 6.9 Hz, 3H), 1.21-1.27 (m, 14H), 1.43 (quint, J = 7.8 Hz, 2H), 1.64 (quint, J = 7.6 Hz, 2H), 2.10 (quint, J = 7.6 Hz, 2H), 3.29 (s, 3H), 3.43 (t, J = 5.2 Hz, 2H), 3.55 (t, J = 5.2 Hz, 2H), 3.61 (t, J = 4.8 Hz, 2H), 3.81 (t, J = 5.6 Hz, 2H), 4.11 (t, J = 5.1 Hz, 2H), 4.25 (t, J = 6.6 Hz, 2H), 4.44 (t, J = 5.2 Hz, 2H), 7.30 (s, 1H), 7.35 (s, 1H), 7.52-7.67 (m, 8H), 8.04 (d, J = 8.4 Hz, 4H), 8.46 (s, 2H), 8.82 (t, J = 7.9 Hz, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150) MHz, CDCl<sub>3</sub>): δ =14.1, 22.7, 26.1, 29.3, 29.6 (3C), 29.6, 29.6, 29.7, 31.9, 58.9, 68.9, 69.5, 69.8, 70.4, 70.6, 70.9, 71.8, 92.4, 92.5, 97.6, 97.6, 114.2, 114.4, 115.7, 115.7, 116.4, 116.4,

117.6, 117.6, 125.7, 126.5, 126.6, 127.1, 127.7, 127.8 (2C), 127.8, 128.6, 128.7, 131.2, 132.6, 153.4, 154.2 ppm. HRMS-EI (*m*/*z*) for C<sub>57</sub>H<sub>60</sub>O<sub>5</sub> [M+] Calcd. 824.4441, found 824.4451. Anal. Calcd. for C<sub>57</sub>H<sub>60</sub>O<sub>5</sub>: C, 82.97; H, 7.33. Found: C, 82.90; H, 7.38.

The **BAB1** was further crystallized from toluene by slow evaporation technique to obtain rhombus-shaped single crystals. X-ray diffraction of the single crystal allowed structure elucidation.

9,9'-((2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-**Synthesis** procedure of divl))dianthracene (BAB2). A sealed-tube was loaded with 1,4-bis(dodecyloxy)-2,5diiodobenzene (516 mg, 739 µmol),<sup>20</sup> 9-ethynylanthracene (374 mg, 1.85 mmol), tetrahydrofuran (20 mL) and triethylamine (2 mL). The resulting solution was degassed with argon thoroughly by freeze-pump-thaw method and then Pd(PPh3)4 (171 mg, 148 µmol) was added. The reaction vessel was again degassed by the same procedure and refluxed for 36 h at 70 °C in oil-bath. Upon cooling to room temperature, red colored precipitate was obtained which was filtered by Whatman 40 filter paper, washed with methanol and dried under vacuum to get BAB2 (532 mg, 85%) as pure compound. FT-IR (KBr pellet,  $4000-400 \text{ cm}^{-1}$ ): 3081 (w), 3054 (m), 2918 (s), 2846 (s), 2189 (w), 1509 (s), 1467 (m), 1483 (s), 1393 (m), 1348 (m), 1278 (m), 1226 (s), 1207 (s), 1120 (s), 737 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta =$ 0.87 (t, J = 6.9 Hz, 6H), 1.22-1.28 (m, 28H), 1.43 (quint, J = 7.8 Hz, 4H), 1.62 (quint, J = 7.6Hz, 4H), 2.12 (quint, J = 7.6 Hz, 4H), 4.26 (t, J = 6.6 Hz, 4H), 7.31 (s, 2H), 7.54 (t, J = 7.6, 4H), 7.62 (t, J = 8.4 Hz, 4H), 8.04 (d, J = 8.4 Hz, 4H), 8.46 (s, 2H), 8.83 (d, J = 8.4, 4H) ppm. HRMS-EI (m/z) for C<sub>62</sub>H<sub>70</sub>O<sub>2</sub> [M+] Calcd. 846.5376, found 846.5381. Anal. Calcd. for C<sub>62</sub>H<sub>70</sub>O<sub>2</sub>: C, 87.90; H, 8.33. Found: C, 87.94; H, 8.18. <sup>13</sup>C NMR measurement was not possible due to insufficient solubility.

Synthesis procedure of 4,4'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2carbaldehyde) (PBMC-open). Synthesis of 4-bromo-5-methylthiophene-2-carbaldehyde, 3-

bromo-5-(diethoxymethyl)-2-methylthiophene and PBMC-open was performed by following literature report (Scheme S3).<sup>21</sup> Herein, a modified synthesis procedure for the last step vielding **PBMC-open** is stated bellow. To a solution of 3-bromo-5-(diethoxymethyl)-2methylthiophene (8.0 g, 28.7 mmol) in THF (80 mL) in a three-necked round-bottomed flask (250 mL), *n*-butyl lithium (2.5 M in hexane, 14.9 mL, 37.3 mmol) was added dropwise at -78 <sup>o</sup>C regulated through thermostat julabo temperature controller and stirred for 1 h at the same temperature under argon atmosphere. Octafluorocyclopentene (1.8 mL, 13.5 mmol) was then added dropwise maintaining the temperature at -78 °C. The resulting mixture was stirred for 4 h and then warmed it up to room temperature. It was stirred at room temperature for 8 h to complete the reaction. The resulting solution was quenched with water (100 mL) and extracted with diethyl ether (3  $\times$  200 mL). The combined organic layer was washed with water (2  $\times$  200 mL), brine (200 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure to obtain the crude product. The crude material was dissolved in THF (150 mL) and then trifluoroacetic acid (6.7 mL, 87.5 mmol) was added dropwise. After 2 h, the reaction mixture was concentrated by rotary evaporator and the solid residue was purified by column chromatography (silica gel, ethylacetate/hexane = 4:1) to afford **PBMC-open** (4.5g, 37%) as light yellow solid. The spectroscopic data matches well with the literature report.<sup>191</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.92$  (s, 6H), 7.51 (s, 2H), 9.86 (s, 2H) ppm. Anal. Calcd. for C<sub>17</sub>H<sub>10</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub>: C, 48.11; H, 2.38; S, 15.11. Found: C, 48.25; H, 2.30; S, 14.88. HRMS-EI (m/z) for C<sub>17</sub>H<sub>10</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> [M+] Calcd. 424.0026, found 424.0043.

**Supporting Information Available:** The Supporting Information is available free of charge on the ACS Publications website.

X-ray crystallography data, CIF file, computational data, FESEM and TEM microscopy, UV-vis, PL, IR, PXRD, and NMR spectra (PDF).

Accession Code. CCDC 1871732 contains the supplementary crystallographic data of BAB1. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing da-ta\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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