Understanding the Electronic Properties of Acceptor–Acceptor′–Acceptor Triads

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Supporting Information

ABSTRACT: In order to develop new organic materials for optoelectronic applications, a fundamental understanding of the electronic properties of specific chromophore combinations must be realized. To that end, we report “model” acceptor (A)–acceptor′ (A′)–acceptor (A) triads in which the pendants (A′) we selected are well-known components of organic optoelectronic applications. Our pendants are sandwiched between two dialkoxyphenazine (A) through an alkyne bond. The A′ was systematically increased in electron-deficiency from benzothiadiazole (BTD-P) to naphthalene diimide with octyl (NDI-O-P) or ethylhexyl groups (NDI-EH-P) to perylene diimide with ethylhexyl (PTCDI-EH-P) to assess changes in the electronic properties of the resultant molecules. Characterizations were performed using both experimental and theoretical methods. From optical and cyclic voltammetry, we found that the electron deficiency of each pendant was directly correlated to the energy level of the lowest unoccupied molecular orbital (E_LUMO). When examining the simple molecular orbital diagrams produced at the B3LYP/6-31G* level of theory, the LUMOs were, as expected, primarily localized on the more electron-deficient pendants. In terms of the energy level of the highest occupied molecular orbital (E_HOMO), the numerical values obtained experimentally also correlated with values obtained computationally. Attempting to construct a simplified model that would explain these correlated values was not as readily apparent, given the disparate physical characteristics of these compounds. For example, BTD-P and NDI-O-P/NDI-EH-P achieved planarity when computationally optimized, but PTCDI-EH-P adapted a “buckled” geometry on the central PTCDI, consequently forcing the attached phenazines out-of-plane. The title compounds showed solvent polarity-dependent fluorescence, which is indicative of intramolecular charge transfer. In conjunction with our theoretical study, the current system can be viewed as an extension of donor–acceptor–donor systems. Thermal properties characterized by differential scanning calorimetry revealed that reversible phase transitions were only observed for BTD-P. In addition, BTD-P was found to be an efficient gelator in 1,1,1-trichloroethane and toluene. The other compounds in this study did not form gels in any of the solvents tested, which may have been a result of the alkyl groups on the pendants hampering the fibrillation process.

INTRODUCTION

Controlling the energy levels of frontier molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), is one of the most important challenges when developing organic π-conjugated materials for optoelectronic applications such as light-harvesting and electron-donating or -accepting. To that end, gaining a fundamental understanding of structure–property correlation is important when attempting to obtain desired electronic properties. Among the strategies to manipulate the electronic properties, an alternating combination of chromophores with electron-donating (D) and -accepting (A) characters may be the most intensively studied molecular configurations, which leads to the formation of charge transfer bands to a lower band gap.1–4 Under this molecular framework, numerous low band gap polymers have been produced mainly as active materials for organic solar cells.5–14 Contrary to polymeric systems, more control over the electronic properties is possible for small and oligomeric systems. More deliberate and complex combinations of different chromophores have led to the creation of configurations such as ADA, DAD, DADAD, and so forth.15–21 With the aid of theoretical calculations, an in-depth understanding regarding how D and A interact to create new energy levels has been made.22,23 However, relatively fewer systematic studies have been conducted on combinations of chromophores with the same electronic character, especially for A–A′–A.24 Understanding the electronic properties of these triads is important as these structural subunits (A and A′)
A’) are the key elements of n-type organic semiconductors. When chromophores with “acceptor-like” electronic character but differing electronic magnitude are connected, it is unclear if the resulting electronic properties follow a simple additivity rule. In a previous study, we prepared acceptor (A’)=acceptor’ (A’)=acceptor (A) triads in which a benzothiadiazole (BTD) (A’) pendant was flanked with two phenazines (A) through two different types of bond connectivity, that is, C–C single and triple bonds.25 To investigate the role of structural subunits on the electronic properties of the whole molecule, we employed a “bottom-up” construction approach, monitoring both the theoretical HOMO and LUMO energy levels for both configurations. One of the key findings from this theoretical analysis was that the more electron-deficient (BTD) dictated the LUMO level of the whole triad. In addition, the C–C triple bond connection rendered a flat molecular geometry for potentially better intermolecular π–π interactions.

In this work, using the A-yn=–A’-yn=–A (A=A=A henceforth) as the basic molecular platform, we prepared four triads with three different types of pendants (A’) to explore the effect of electron-withdrawing power of each pendant on the electronic properties of each triad. Using BTD as a standard, we modified the pendants to be stronger electron-acceptors, naphthalene diimide (NDI) and perylene diimide (PTCDI). Detailed synthetic approaches for new A–A’–A triads as well as their optical, electrochemical, and thermal properties are presented. Theoretical investigations on the energy levels, molecular orbital diagrams, and optimized geometries were conducted to complement the experimental observations. Finally, self-assembly of these compounds was tested through organogelation.

## RESULTS AND DISCUSSION

### Synthesis

The structures of title compounds are presented in Figure 1 and detailed synthesis is described in the Supporting Information.

**Figure 1.** Molecular structures of title A–A’–A triads.

**Supporting Information.** The key reaction step to produce the title compounds was a Sonogashira coupling reaction between intermediate 7-ethynyl-2,3-bis(octxylo)phenazine (6) and dibromo-pendant (pendant = BTD, NDI-ethylhexyl, NDI-octyl, and PTCDI-ethylhexyl).

The first step in synthesizing the crucial intermediate 6 was nitration of m-iodonitrobenzene.26 This nitration yielded 1-iodo-3,4-dinitrobenzene (1), which was then reduced using Sn over HCl to yield 1-iodobenzene-3,4-diamine (2).27 Then, the diamine was reacted with 2,5-dihydroxy-1,4-benzoquinone in ethanol to produce 7-iodo-2,3-bis(hydroxy)phenazine (3), which was further alkylated without purification. 7-Iodo-2,3-bis(octxylo)phenazine (4) was then used in a Sonogashira coupling reaction with triisopropylsilylethynyl (TIPS) acetylene to yield 7-trisopropylsilylethynyl-2,3-bis(octxylo)phenazine (5). Then, TIPS was removed using tetrabutylammonium fluoride to yield intermediate 6. Intermediate 6 was employed for Sonogashira coupling reactions with corresponding dibromo-pendants, which successfully produced the title compounds. The dibromo-pendants (4,7-dibromo-2,1,3-benzothiadiazole, di-(2-ethyl-1-hexyl)-2,6-dibromo-1,4,5,8-napthalenetetracarboxylic acid bisamide, dioctyl-2,6-dibromo-1,4,5,8-napthalenetetracarboxylic acid bisamide, and di-(2-ethyl-1-hexyl)-1,7-dibromo-3,4,9,10-perylenetetracarboxylic acid bisamide) were synthesized according to the reported procedures.

The final compounds could alternatively be prepared by coupling reactions between 7-iodo-2,3-bis(octxylo)phenazine (4) and diethynyl-pendants; however, we chose the current routes because of the following two reasons; (i) diethynyl-pendant was very unstable and (ii) the number of reaction steps are fewer with the current routes. We note that the alternative route using 4,7-diethynyl-2,1,3-benzothiadiazole was employed to prepare BTD-P with different alkyl lengths in the previous communication.25 However, we found that the reaction yield was inconsistent when 4,7-diethynyl-2,1,3-benzothiadiazole was not carefully treated.

Under the typical Sonogashira coupling reaction conditions (see Scheme S1), BTD-P was obtained in 43% yield. However, the reaction conditions needed to be modified for NDI-P molecules. For NDI-EH-P, when the reaction was conducted at 70 °C overnight, the initially formed bright red solution turned to dark brown. A thin-layer chromatography (TLC) analysis indicated that the initially formed product (red solid) had been decomposed. The reaction seemed to be highly sensitive to time and temperature. Therefore, further trial was carried out at room temperature and the reaction progress was closely monitored using TLC. The maximum conversion was observed after 1.5 h of reaction, and NDI-EH-P was obtained in 64% yield. In the case of NDI-O-P and PTCDI-EH-P, the coupling reaction was also conducted at room temperature for 2.5 and 5 h, respectively.

Unlike other compounds, the purification of PTCDI-EH-P was extremely difficult, requiring both silica gel and neutral alumina column chromatography, with a yield of 28%. The structures and purity of BTD-P, NDI-EH-P, NDI-O-P, and PTCDI-EH-P were confirmed by 1H NMR, 13C NMR, and high resolution-mass spectrometry (Supporting Information).

### Optical Properties

The UV–visible absorption spectra were obtained for all title compounds in both solution and solid states (Figure 2). For solution in dichloromethane (DCM), all the peaks showed a linear relationship with concentration (1–5 μM), confirming that the absorption was free of aggregation. The absorption maximum (λmax) for BTD-P was observed at 445 nm. Both NDI-EH-P and NDI-O-P showed longer wavelength absorption at 514 nm, and the longest λmax of 587 nm was seen with PTCDI-EH-P. It should be noted that the absorption patterns of NDI-EH-P and NDI-O-P are essentially identical, suggesting that the alkyl chain does not contribute to the absorption. The red shift in the absorption can be translated into a reduced HOMO–LUMO energy gap (Egap), and the degree of such shift becomes higher as the electron-deficiency of the pendant increases from BTD to NDI to PTCDI. Whether the electron-deficiency of the
pendant plays a major role in the reduction of $E_{\text{gg}}$ will be investigated in greater detail.

The molar absorptivity ($\varepsilon$) for the title compounds at their $\lambda_{\text{max}}$’s were calculated from the slope of the Beer's law plots. These values are summarized in Table S1 (Supporting Information). BTD-P, NDI-EH-P, and NDI-O-P showed similar absorptivity at 7 to $8 \times 10^{4}$ M$^{-1}$ cm$^{-1}$. However, the molar absorptivity for PTCDI-EH-P was somewhat lower with $\varepsilon = 2.9 \times 10^{4}$ M$^{-1}$ cm$^{-1}$.

$E_{\text{gg}}$ for the title molecules was calculated from the absorption edge (Table 1). A trend in smaller $E_{\text{gg}}$ as the electron deficient pendant, gave the largest $E_{\text{gg}}$ of 2.51 eV. NDI-EH-P and NDI-O-P with more electron-deficient pendants showed $E_{\text{gg}}$ of 2.23 eV. The title molecule with the most electron-deficient pendant, PTCDI-EH-P, gave the smallest $E_{\text{gg}}$ of 1.97 eV.

For the solid-state absorption, samples were prepared as a cast film from DCM solution. Their resulting spectra were compared with those in solution as shown in Figure 2. The cast films showed similar absorption patterns when compared to their solution counterparts. However, all the cast film spectra showed a significantly red-shifted $\lambda_{\text{max}}$ from their respective solution spectrum, which could be attributed to the formation of J-aggregates. For BTD-P, the shoulder peak of $\lambda_{\text{max}}$ at 462 nm in solution was red-shifted to 489 nm in the solid state; however, the peak at 445 nm in solution was slightly blue-shifted. For NDI-EH-P and NDI-O-P, $\lambda_{\text{max}}$ at 514 nm in solution was red-shifted to 545 nm in the solid phase. The largest red shift of 36 nm was seen for PTCDI-EH-P with $\lambda_{\text{max}}$ at 623 nm in the solid phase.

The fluorescence (FL) spectra were obtained for BTD-P, NDI-EH-P, NDI-O-P, and PTCDI-EH-P in DCM. The spectra shown in Figure 3 compare the FL emission maxima ($\lambda_{\text{em}}$) of the title compounds. As in the case of absorption, the concentration from the emission study was kept at 5 $\mu$M in DCM, which follows Lambert Beer’s Law to avoid emission from aggregates. The resulting spectra were normalized for better comparison.

As shown in Figure 3, $\lambda_{\text{em}}$ was significantly red-shifted going from BTD-P to NDI-EH-P/NDI-O-P, and then a less dramatic red shift for PTCDI-EH-P. This was a different trend when compared to the consistent absorption shift in the UV–vis. PTCDI-EH-P showed the longest $\lambda_{\text{em}}$ of 622 nm, however with the smallest Stokes shift of 35 nm. NDI-EH-P and NDI-O-P showed $\lambda_{\text{em}}$ of 591 nm, with a Stokes shift of 77 nm. BTD-P showed $\lambda_{\text{em}}$ of 508 nm, with a Stokes shift of 63 nm. Absolute FL quantum yields measured using an integrating sphere for BTD-P and PTCDI-EH-P were quite high, 61 and 54%, respectively. On the contrary, both NDI-EH-P and NDI-O-P showed only 8%.

Figure 3 also shows the solid-state emission spectra of BTD-P, NDI-EH-P, and NDI-O-P. PTCDI-EH-P underwent a significant aggregation-induced emission quenching, and thus the emission in the solid state became negligible. All three compounds experienced red-shifted emission in the solid state compared to their solution state. $\lambda_{\text{em}}$ for BTD-P, NDI-EH-P, and NDI-O-P was 580, 641, and 628 nm, respectively. The degree of red shift from solution in the same order was found to be 72, 50, and 37 nm, respectively. Albeit small, it is interesting that the NDI-EH-P film emits a 13 nm longer wavelength than NDI-O-P. Overall, the red-shifted emission in the solid state corroborates well with the result of UV–vis absorption spectroscopy. Both characterizations support the formation of J-aggregates in the film.

We also examined the emission in solvents with different polarity such as toluene, THF, and chloroform in addition to DCM. For this study, NDI-EH-P was omitted because of limited solubility in THF and toluene. Interestingly, all three compounds showed a positive solvatochromism as shown in Figure 4. $\lambda_{\text{em}}$ of all three compounds red-shifted as the polarity of solvent increased. $\lambda_{\text{em}}$ in each solvent is summarized in

Table 1. Summary of Electronic Properties

| Compound       | $E_{\text{HOMO}}$(eV) | $E_{\text{LUMO}}$(eV) | $E_{\text{g}}$(eV) | $E_{\text{gg}}$(eV) | $E_{\text{em}}$(eV) | $E_{\text{E}}$(eV) |
|----------------|-----------------------|-----------------------|-------------------|-------------------|--------------------|------------------|
| BTD-P          | -3.34                 | -5.85                 | 2.51              | -2.75             | -5.30              | 2.55             |
| NDI-EH-P       | -3.90                 | -6.13                 | 2.23              | -3.29             | -6.61              | 2.32             |
| NDI-O-P        | -3.90                 | -6.13                 | 2.23              | -3.29             | -6.61              | 2.32             |
| PTCDI-EH-P     | -3.97                 | -5.94                 | 1.97              | -3.37             | -5.48              | 2.11             |

*aFrom cyclic voltammetry. $E_{\text{HOMO}}^\text{exp} = E_{\text{LUMO}}^\text{exp} - E_{\text{g}}$. *bFrom UV–vis. *cCalculated using B3LYP/6-31G*. $E_{\text{E}} = E_{\text{HOMO}}^\text{exp} - E_{\text{LUMO}}^\text{exp}$.
Figure 4. FL spectra of BTD-P, NDI-O-P, and PTCDI-EH-P in solvents with different polarities. \( \lambda_{\text{em}} \): 425 nm for BTD-P, 490 nm for NDI-O-P, and 540 nm for PTCDI-EH-P.

Table S2. From toluene to DCM, \( \lambda_{\text{em}} \) of BTD-P red-shifted by 13 nm. For NDI-O-P, the red shift was the most significant, 41 nm. PTCDI-EH-P showed the smallest red shift of 7 nm. This positive solvatochromism indicates intramolecular charge transfer (ICT).

Electrochemical Properties. The effect on electrochemical properties by changing the electron deficiency of the pendant on the title molecules was examined using cyclic voltammetry. The compounds were tested in a DCM solution with TBAPF_6 (0.1 M) as the supporting electrolyte, Ag/AgNO_3 in CH_3CN as the reference electrode, and ferrocene as an internal reference. The resulting cyclic voltammograms are shown in Figure 5. All molecules showed three reduction peaks. The first two reductions originate from the pendants, showing a similar pattern to the reported ones, especially for PTCDI-P and NDI.

As shown in Figure 5, the onset of the first reduction peak decreased in energy as the pendant of the title molecules became more electron-deficient. BTD-P gave the highest \( E_{\text{LUMO}} \) of \(-3.34\) eV (F_{\text{onset}} = -1.46 V). The trend continues with NDI-EH-P/NDI-EH-P showing a significantly more stabilized \( E_{\text{LUMO}} \) of \(-3.90\) eV (F_{\text{onset}} = -0.90 V). The lowest \( E_{\text{LUMO}} \) is seen from PTCDI-EH-P at \(-3.97\) eV (F_{\text{onset}} = -0.83 V), however, only slightly less than the \( E_{\text{LUMO}} \) of NDI-EH-P and NDI-O-P. In conjunction with UV–vis spectroscopy, \( E_{\text{opt}}^{\text{red}} \) compression was clearly influenced by \( E_{\text{LUMO}} \) stabilization; however, it warrants a closer analysis.

For our calculations, we replaced all extended alkyl chains with methyl groups. Our general interest is observing energy trends, and we have found in previous work that these trends are not impacted by such a simplification. We note that NDI-P refers to both NDI-O-P and NDI-EH-P, and PTCDI-P refers to PTCDI-EH-P for theoretical calculation. From our observations of the larger molecular systems, it was clear that \( E_{\text{LUMO}} \) was controlled by the electron-deficient pendant. In the case of BTD-P, \( E_{\text{LUMO}} \) was more stabilized than either P or BTD as individual units. For NDI-P, the central pendant’s

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had a dihedral angle of 0°. In the case of PTCDI-P, $E_{\text{LUMO}}$ was nearly equivalent to that of the central pendant (PTCDI). An inspection of LUMO orbital diagrams (Figure 7) for all systems studied validates these observations. For all compounds, the LUMO orbitals were localized on the pendant and thus electron-deficiency of the pendant was reflected in $E_{\text{LUMO}}$'s of the whole molecules.

In contrast, HOMO orbitals for all compounds were distributed to a more or lesser degree over the entire molecule including the phenazines. For example, the HOMO orbital of BTD-P was delocalized throughout the molecule, albeit with more concentration on the central unit and alkyne portion. A somewhat similar pattern was observed for PTCDI-P; however, the orbital was distributed less on phenazine. In contrast, the HOMO of NDI-P was distributed more on the alkyne and phenazine. Thus, the HOMO energies were not influenced in these simple density functional calculations by the most electron-withdrawing portion of pendant, that is, thiadiazole for BTD and imide for NDI and PTCDI. Therefore, the electron-deficiency of the pendant did not play as significant a role in defining $E_{\text{HOMO}}$ as it did for $E_{\text{LUMO}}$ for all systems considered in this work.

The energy-minimized structures of both BTD-P and NDI-P were planar (Figure 8). However, PTCDI-P exhibited a "puckered" shape when optimized. BTD-P and NDI-P both had a dihedral angle of 0° between A–A’–A, whereas PTCDI-P had a puckered angle of 17.20°. The nonplanarity of PTCDI may be due to the steric repulsion between C≡C and neighboring H on the pyrene. We conclude that the more electron-deficient pendants control $E_{\text{LUMO}}$ values, whereas $E_{\text{HOMO}}$ is influenced by a multitude of factors including subunit connectivity and the overall geometry of the extended system. Therefore, the ability to manipulate the LUMO energy of such extended systems is easily controlled by proper choice of an electron-deficient subunit, whereas the ability to strategically influence the HOMO energy of such systems remains elusive.

The localization of the LUMO on the more electron-deficient unit is reminiscent of those found in D–A systems. Heteroaromatic systems with electron-deficient C≡N bond such as quinoline, quinoxaline, phenazine, and so forth have been used as electron-acceptors for light-emitting diodes. However, there is no absolute definition for an acceptor or a donor. The electronic role of a structural unit is determined by the relative electron-accepting or -donating power of the neighboring unit. For example, when a quinoline is sandwiched between two thiophenes, phenazine acts as an acceptor with the LUMO localization on the phenazine. In the current system, phenazine may act as a weak donor because of the presence of stronger electron-accepting BTD, NDI, or PTCDI. In a sense, our A–A’–A system can be regarded as an extended donor–acceptor–donor system in which ICT is possible. Indeed, ICT was well supported by the FL solvatochromism. The level of ICT was clearly higher in the case of NDI-O-P than BTD-P because of the higher electron-accepting power of NDI than BTD. However, in spite of the strongest electron-accepting pendant, PTCDI-EH-P exhibited the lowest level of ICT. Presumably, this is due to the nonplanarity of the molecule limiting π-electron delocalization.

The predictive power of computation when it involves identifying trends in $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ for all molecules studied was invaluable. Clearly, these computationally simplistic orbital diagrams as well as optimized geometries provide greater insight into these observed physical properties. For example, the unusually high experimental $E_{\text{HOMO}}$ of PTCDI-EH-P relative to those of other molecules was clearly predicted by the theory. This result demonstrates that theoretical evaluation serves as a crucial tool in our research for a more complete understanding of our results.

**Thermal Properties.** The thermal properties of BTD-P, NDI-EH-P, NDI-O-P, and PTCDI-EH-P were studied by differential scanning calorimetry (DSC). Of the four title compounds, BTD-P was the only one that showed reversible phase transitions (Figure S1). The second heating/cooling scan is presented in order to eliminate any transition because of a pre-existing nonintrinsic molecular arrangement. A melting endotherm ($T_m$) was observed at 178 °C with a heat of melting ($\Delta H_m$) of 45.65 J/g. At the cooling scan, a crystallization exotherm ($T_c$) appeared at 171 °C.

Unlike BTD-P, the remaining compounds showed irreversible thermal transition, and therefore only the first heating

**Figure 7.** Molecular orbital diagrams of title compounds: (a) BTD-P; (b) NDI-P; (c) PTCDI-P.

**Figure 8.** Energy-minimized structures of (a) BTD-P, dihedral angle = 0°; (b) NDI-P, dihedral angle = 0°; (c) PTCDI-P, puckered angle = 17.20°; (d) alternate view of PTCDI-P.
scan is shown in Figure 9. NDI-EH-P showed a $T_m$ at 254 °C with a $\Delta H_m$ of 25.73 J/g. NDI-O-P showed a lower $T_m$ at 222 °C with a larger $\Delta H_m$ of 33.54 J/g. In spite of the largest π-core, PTCDI-EH-P showed the lowest $T_m$ at 192 °C with a $\Delta H_m$ of 29.92 J/g. For all three compounds, there were additional exotherms positioned shortly after $T_m$. These exotherms are likely a result of a possible cyclization reaction occurring between the triple bonds and the carbonyl groups in NDI or aromatic rings in PTCDI. Our attempt to characterize the materials after the DSC experiment was unsuccessful as the materials after thermal treatment were intractable.

We initially expected NDI-EH-P would have a lower $T_m$ than NDI-O-P as ethylhexyl is bulkier than the octyl group, which would hamper the π–π interaction. However, the results indicated otherwise. The longer octyl group reduced $T_m$ more than the bulkier but shorter ethylhexyl. Nevertheless, it should be noted that the straight octyl group of NDI-O-P facilitates better molecular packing and thus crystallization revealed by the larger $\Delta H_m$. The low $T_m$ of PTCDI-EH-P is consistent with the nonplanar geometry predicted by theory, which limits intermolecular interactions.

**Organogelation.** In our molecular design, the dialkoxyphenazine (A) unit was included not only to control certain electronic properties, but to promote self-assembly as well. Assembly properties are important for organic conjugated molecules as solid-state properties are largely affected by molecular organization. Organogelation is a simple and reproducible way to prepare one-dimensional (1D) fibers via nonbonding intermolecular forces such as hydrogen bonding, π–π, and van der Waals interactions. We anticipated that including dialkoxyphenazine in the title compounds would facilitate organogelation, as dialkoxyphenazine has been known to be an efficient gelator. When comparing the title compounds, the pendant in BTD-P is the only unit without an alkyl group which would not interfere with fibrillation driven by dialkoxyphenazine. The remaining compounds contain alkyl side groups on the pendants, and it is unclear if the alkyl side groups on the pendants support or interfere with fibrillation. To test organogelation, the compounds were suspended in solvent at known concentrations and then heated until they were fully dissolved. The solutions were then left undisturbed as they cooled to room temperature and observed for the formation of a gel. When turning the vial upside down, successful gelation was identified if there was no flow of solution, which is evidence of solvent-trapping in a 3D network of 1D fibers. The gelation properties in select solvents are summarized in Table 2.

**Table 2. Gelation Properties of Title Compounds**

|       | BTD-P | NDI-EH-P | NDI-O-P | PTCDI-EH-P |
|-------|-------|----------|---------|------------|
| CHCl₃ | S     | S        | S       | S          |
| CHCl₂ | S     | S        | S       | S          |
| TCTFE | PPT   | NS       | NS      | PPT        |
| CCl₄  | PPT   | PPT      | S       | S          |
| DCE   | PPT   | PPT      | PPT     | S          |
| TCE   | G (5 mM) | PPT | S    | S          |
| EA    | PPT   | NS       | NS      | S          |
| THF   | S     | PPT      | S       | S          |
| hexane| PPT   | NS       | NS      | S          |
| cyclohexane | PPT | NS       | PPT     | S          |
| toluene| G (6 mM) | PPT | S    | S          |

*Abbreviations: G, gel; PPT, precipitation after cooling; S, soluble after cooling; NS, not soluble; DCE,1,2-dichloroethane; TCTFE, 1,1,2-trichloro-2,2,1-trifluoroethane; TCE, 1,1,1-trichloroethane; EA, ethyl acetate; THF, tetrahydrofuran. Critical gelation concentration is shown in parentheses.*

Various types of solvents were tested including nonpolar hydrocarbon, aromatic, polar, and halogenated solvents. It was found that BTD-P was the only efficient gelator which gelled TCE (5 mM) and toluene (6 mM). The fact that other compounds lack the fibrillation capability suggests that the alkyl groups in the pendants interfere with fibrillation. Note that PTCDI-EH-P was soluble in all of the solvents tested in spite of the large pendant. This may be due to the non-flat nature of the molecule causing ineffective intermolecular organization.

To investigate the morphology, field-emission scanning electron microscopy (FE-SEM) characterization was conducted on the xerogel of BTD-P. The xerogel was prepared by drying a TCE gel. At a low magnification (Figure 10A), fiber-like structures were observed. However, the thickness of the fibers was too large, considering the transparency of the TCE gel (Figure 10A inset). Presumably, the structures were formed during the solvent vaporization. We attempted to identify individual fibers at a higher magnification. As shown in Figure 10B, silhouettes of fused fibers were observed; however, we were unable to have a better focus because of the lack of sharp fiber edges. We believe the thin soft fibers formed in organogel lost their fine structures during solvent vaporization producing fused fibers.
CONCLUSIONS

In this work, we have successfully synthesized and characterized four A−A′−A triads with varying electron-deficiency of the pendants A′. Optical and cyclic voltammetry characterizations revealed that the increasing electron-deficiency of pendants from BTD to NDI to PTCDI lowered \( E_{\text{LUMO}} \) albeit to different degrees. Nevertheless, \( E_{\text{LUMO}} \) was reduced steadily from BTD-P to NDI-EH-P/NDI-O-P to PTCDI-EH-P. This is due to the contributions of each molecule’s \( E_{\text{HOMO}} \) which changed rather randomly. Computational analysis indicated that the LUMO orbitals were localized on the pendants; consequently, \( E_{\text{LUMO}} \) energies were virtually controlled by the pendants. Theoretical characterizations revealed that BTD-P and NDI-P adapted planar geometries, whereas PTCDI-P optimized to a puckered configuration likely because of steric repulsions between the alkylene carbon and the neighboring hydrogen on PTCDI. This nonplanar geometry contributed to the HOMO orbital localizing on the pendant and the pyrene units as opposed to the attached phenazines. In contrast to the simplicity of our LUMO energies, the HOMO energies for our molecules were more difficult to explain, presumably because there were more parameters involved in defining this energy including overall molecular structure, subunit connectivity, and so forth. FL solvatochromism was observed for the title compounds which is indicative of ICT. Although the present systems contain apparent electron-acceptors, based on the ICT and LUMO orbital distribution, they can be viewed as an extension of a donor–acceptor–donor system because of the difference in the electron-deficiency of A and A′. It seems that the electronic role of certain structural subunits is determined by the relative electron-accepting power of a neighboring unit. DSC characterization revealed that only BTD-P possessed reversible phase transition. In addition, BTD-P was found to be the only gelator in TCE and toluene. For other compounds, alkyl side groups on pendants may have interfered with fibrillation.

The structurally simple triads in this work serve as a model system for shedding light on basic physical properties when chromophores with different electron deficiencies combine. Correlation between experiment and theory provides a deeper understanding into our observations although there are still complexities regarding certain physical properties (HOMO energies) that defy a simple explanation. Further studies with a greater variety of systems would be necessary to elucidate the governing factors to control \( E_{\text{HOMO}} \).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03554.

Detailed synthetic procedures, DSC thermogram of BTD-P, molar absorptivity of title compounds, and \( \lambda_{\text{em}} \) of BTD-P, NDI-O-P, and PTCDI-EH-P in different solvents (PDF)

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Author Contributions

The article was written through the contributions of all the authors. All the authors have given approval to the final version of the article.

Notes

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