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# Vapor-Phase Detection of Trinitrotoluene by AIEE-Active Heterooligophenylene-Based Carbazole Derivatives

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### **Supporting Information**

**ABSTRACT:** New AIEE-active hetero-oligophenylene carbazole derivatives **3** and **4** have been synthesized and serve as fluorescent probes for the selective detection of 2,4,6-trinitrotoluene (TNT) in the vapor phase, the solid phase, and aqueous media. In addition, paper strips prepared by dipcoating a solution of aggregates of derivatives **3** and **4** can provide a simple, portable, sensitive, selective, low-cost method for the detection of TNT on the picogram level.



# INTRODUCTION

Trinitroaromatics are well-known primary constituents of many unexploded land mines worldwide<sup>1</sup> and are also considered to be environmental contaminants because the soil and groundwater of war zone and military facilities can contain toxic level of these compounds. Trinitrotoluene (TNT), a widely used nitroaromatic explosives, is poisonous and carcinogenic and can adversely affect male fertility.<sup>2</sup> TNT can also cause skin irritation, anemia, and abnormal liver function.<sup>2</sup> Therefore, the development of cost-efficient, selective, sensitive, portable detection methods for TNT is highly desirable. Although several strategies using quantum dots,<sup>3</sup> gold nanoparticles,<sup>4</sup> silver-gold alloy nanostructures,<sup>5</sup> and molecular imprinting with AuNP's<sup>6</sup> have been reported, no single strategy incorporating all of the above-mentioned features has been reported. Recently, there has been a lot of activity with respect to the preparation of conjugated polymers<sup>7</sup> and fluorescent nanofibers<sup>8</sup> for the efficient detection of nitroaromatic compounds. However, real-time monitoring of the polymeric materials is limited because of their multistep conventional covalent synthesis. Furthermore, most of these reported sensors exhibit a more sensitive response toward dinitrotoluene (DNT) than toward to TNT. Thus, the development of highly selective, sensitive, fluorescent sensor materials for the detection of TNT at low concentration is still a challenge.<sup>9</sup>

Recently, AIE(E)-active materials have been used as sensors for the detection of nitroaromatics.<sup>10</sup> AIE(E)-active lowmolecular-weight luminogens are beneficial because they offer more diffusion channels for the exciton to migrate, allowing them to be more quickly anihilated by explosive quenchers.<sup>10a</sup> Keeping this in mind, we planned to prepare AIEE-active material for the selective sensing of TNT. Thus, we designed and synthesized new hetero-oligophenyl-based derivatives **3** and **4** having the carbazole moiety. We have chosen the carbazole moiety for its good electroluminescence and holetransporting properties. Interestingly, derivatives **3** and **4** exhibit AIEE characterstics and good selectivity for TNT over other nitroaromatics such as 2,4-dinitrotoluene (DNT), 1,3-dinitrobenzene (DNB), and picric acid (PA). Disposable paper strips prepared by dip-coating solutions of aggregates of derivatives **3** and **4** can detect TNT on the picogram level, thus providing a simple, low-cost method for the detection of TNT in aqueous solution. To the best of our knowledge, AIEE-active hetero-oligophenyl carbazole derivatives that sense TNT in the vapor phase, solid phase, and aqueous phase and uphold good selectivity for TNT over DNT are unprecedented in the literature. Furthermore, AIEE-active derivatives **3** and **4** exhibit a more sensitive response toward TNT than do previously reported chemosensors for TNT.<sup>11</sup>

## RESULTS AND DISCUSSION

The reaction of carbazole acetylene derivative  $1a^{12}$  with 3,4bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone  $2^{13}$ in diphenylether furnished compound 3 in 82% yield (Scheme 1). Using the same synthesis procedure as used for 3, we also prepared compound 4 by heating carbazole phenyl acetylene derivative  $1b^{14}$  with 4-bis(4-methoxyphenyl)-2,5 diphenylcyclopenta-2,4-dienone 2 in 81% yield (Scheme 1). The structures of compounds 3 and 4 were confirmed from their spectroscopic and analytical data (Supporting Information, Figures S13–S18).

The UV–vis spectrum of compound 3 in THF exhibits absorption bands at 271 and 290 nm. However, in the presence of 80%  $H_2O$  in THF, the absorption bands were observed at 240 and 305 nm, which are attributed to the aggregate state of compound 3. In the visible spectral region of the absorption

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Scheme 1. Synthesis of Derivatives 3 and 4



spectrum of 3 (8:2  $H_2O/THF$ ), a leveling-off tail was observed (Supporting Information, Figure S2) which is due to the nanoparticle suspensions, confirming the existence of aggregates of 3 in the solvent mixture (8:2  $H_2O/THF$ ).<sup>15</sup> The formation of aggregates of derivatives 3 and 4 is supported by scanning electron microscopy (SEM) images of derivatives 3 and 4 in 8:2  $H_2O/THF$ , which show the presence of spherical aggregates (Figure 1).



Figure 1. Scanning electron microscopy (SEM) images of aggregates of compounds (A) 3 and (B) 4 in 8:2  $H_2O/THF$ .

In the fluorescence spectrum, compound 3 exhibits weak emission ( $\phi_0 = 0.0018$ )<sup>16</sup> at 363 nm when excited at 290 nm (Figure 2). However, on addition of an 80% volume fraction of



**Figure 2.** Fluorescence emission spectra of 3 (1  $\mu$ M) for different H<sub>2</sub>O/THF ratios.  $\lambda_{ex}$  = 290 nm. The inset shows the difference in fluorescence for 3 in (i) THF and (ii) H<sub>2</sub>O/THF.

water, the emission band at 363 nm shows a maximum enhancement ( $\phi_{AIEE} = 0.59$ ). The increase in the fluorescence of compound 3 in 80% H<sub>2</sub>O in THF with respect to that in pure THF can also be seen by the naked eye (inset of Figure 2). Under the same set of conditions, similar absorption and emission behavior was observed for 4 ( $\phi_0 = 0.006$ ,  $\phi_{AIEE} = 0.43$ ; Supporting Information, Figures S1 and S3). When the water fraction is higher than 80%, the solubility of derivatives 3 and 4 in the solvent mixture is relatively low and the number of emissive molecules per unit volume is decreased. The fluorescence enhancement due to the restriction-in-rotation process could not contend with the decreasing trend in the intensity caused by the smaller number of emitting molecules. Hence, the fluorescence intensity is decreased.<sup>17</sup>

We believe that in aqueous media intramolecular rotations are restricted by the formation of aggregates that block the nonradiative channels and populate the radiative excitons, thereby making the molecule emissive in the aggregate state. We envisioned that if this mechanism is indeed at work then the solution of compounds 3 and 4 should become more emissive when the viscosity is increased because the thickening process is known to hamper intramolecular rotations.<sup>18</sup> Thus, we recorded the fluorescence spectra of compounds 3 and 4 in highly viscous triethylene glycol (TEG), and the spectra show much higher emission than that in THF (Supporting Information, Figure S4). The concentration-dependent emission studies of compounds 3 and 4 in THF also support the enhancement in emission upon aggregation that is due to restricted intramolecular rotations (Supporting Information, Figures S5 and S6). We carried out the concentration dependent <sup>1</sup>H NMR studies of both compounds 3 and 4 (Supporting Information, Figures S20 and S21). In both cases, an average downfield chemical shift of 0.08 ppm is observed in aromatic protons and is attributed to the greater deshielding of aromatic protons due to the restriction in rotation caused by intermolecular aggregation.<sup>19</sup> Derivative 4 has one additional rotor in comparison to 3, which sterically hinders the rotation of rotors around their axes in 4, which is clearly evident from the smaller quantum yield obtained for derivative 3 as compared to that obtained for compound 4. Therefore, the extent of rotation of rotors in compound 4 is already low as compared to that in compound 3. Therefore, the degree of restriction in the rotation of the rotors is relatively greater for compound 3 as compared to that for compound 4. Therefore, the extent of AIEE is greater in compound 3 as compared to that in compound 4.

Furthermore, to investigate the properties of **3** and **4** as AIEE-active materials for the recognition of nitroaromatics, we studied the fluorescence behavior of **3** and **4** toward different nitro compounds, viz., 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), picric acid (PA), 1,4-dintrobenzene (DNB), *p*-nitrotoluene (PNT), *p*-nitrobenzene (PNB), *p*-nitrophenol (PNP), 2,3-dinitro-2,3-dimethyl butane (DNDMB)}, and two reference aromatic compounds (benzoic acid (BA) and benzoquinone (BQ)).

It was observed that on addition of 10  $\mu$ M TNT to the solution of 3 (Figure 3) and 13  $\mu$ M TNT to the solution of 4

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**Figure 3.** Change in the fluorescence of 3 (1  $\mu$ M in 8:2 H<sub>2</sub>O/THF) on adding 10  $\mu$ M TNT. The inset shows the difference in the fluorescence of 3 (i) before and (ii) after adding TNT to H<sub>2</sub>O/THF.

(Supporting Information, Figure S7), 94 and 92% quenching of fluorescence emission was observed, respectively (Figure 4).



Figure 4. Selectivity graph of 3 and 4 toward TNT for 10 and 13  $\mu$ M analyte, respectively. The inset shows the Stern–Volmer plot of % quenching vs TNT concentration.

The quenching of fluorescence in compound **3** (8:2 H<sub>2</sub>O/ THF) upon the addition of TNT can also be observed by the naked eye (inset of Figure 3). The detection limits of **3** and **4** as fluorescent sensors for TNT are found to be  $30 \times 10^{-9}$  and  $40 \times 10^{-9}$  mol L<sup>-1</sup>, respectively (Supporting Information, Figures S10 and S11), which are low enough for the detection of submillimolar concentrations of TNT. We also investigated the emission behavior of **3** in pure THF in the presence of 10  $\mu$ M TNT, where only a 40% quenching of fluorescence emission was observed (Supporting Information, Figure S17). This finding demonstrates the utility of aggregates in the detection of TNT.

The Stern–Volmer plots of aggregates **3** and **4** are linear (inset of Figure 4) and give quenching constants  $(K_{SV})^{20}$  of  $13.3 \times 10^5$  and  $10.0 \times 10^5$  M<sup>-1</sup>, respectively. These Stern–Volmer constants are considerably larger than those in previous reports.<sup>11,21</sup> We propose that the quenching of fluorescence of aggregates of **3** on addition of nitroaromatics is ascribed to the static quenching. The normalized overlays of the absorption spectrum of TNT and emission spectra of **3** and **4** do not show any significant overlaps (Supporting Information, Figures S12 and S13), which indicates that the main quenching mechanism for TNT is charge transfer between the higher-energy state of the host and the lower-energy state of the TNT.

A tail was found in the UV–vis spectra of compound 3 on addition of 20  $\mu$ M TNT. The formation of this tail is probably due to the interaction between aggregates of 3 and TNT, which can facilitate the charge transfer between them.<sup>10a</sup> Similar

behavior was observed for compound 4 (Supporting Information, Figures S14 and S15). The charge-transfer mechanism was further confirmed by cyclic voltammetry. The higher energy of the LUMO (lowest unoccupied molecular orbital, -3.56 eV) of 3 allows the electron to jump to the lower-energy LUMO of TNT  $(-3.7 \text{ eV})^{10a}$  (Supporting Information, Figure S16).

To verify the charge-transfer mechanism, we also recorded the <sup>1</sup>H NMR of derivative **3** after adding 2 equiv of TNT (Supporting Information, Figure S19). The average downfield shift of 0.08 ppm in all signals was observed, which validated the charge transfer between compound **3** and TNT.

The quenching of fluorescence emission with different compounds tested follows the order TNT > DNT > PA > DNB > PNT > NB > PNP (Supporting Information, Figures S8 and S9). No change in fluorescence emission was observed on addition of BA and BQ, which demonstrates that recognition behavior is observed with respect to nitro compounds only (Figure 4). It is evident from the results that the most electron-deficient aromatic substrate engendered the greatest quenching. This finding is consistent with the proposed mechanism in which a nitroaromatic analyte acts as a fluorescence quencher as a result of a charge-transfer event.

The charge-transfer mechanism is more assisted in quenching derivatives **3** and **4** with TNT because the lowerenergy LUMO (lowest unoccupied molecular orbitals) of TNT (-3.7 eV) is much lower than that of other nitroaromatics (e.g., 2,4-dinitrotoluene (DNT, -3.5 eV), nitrobenzene (DNB, -3.35 eV), etc.<sup>22</sup>). Thus, the higher energy of the LUMO (-3.56 eV) of **3** allows the electron to jump to the lowerenergy LUMO of TNT more easily than to the lower-energy LUMO of other nitroaromatics.

For the detection of TNT vapors, we exposed a solution of 3 and 4 in 8:2  $H_2O/THF$  to vapors of TNT by inserting the vial containing the solution into a sealed vial containing solid trinitrotoluene at room temperature. The 25 and 22% quenching of 3 (Figure 5) and 4 (Supporting Information,



**Figure 5.** Change in fluorescence of 3 (1  $\mu$ M in 8:2 H<sub>2</sub>O/THF) on exposing to the vapors of solid 2,4,6-trinitrotoluene after 0, 1, 5, 10, 15, 20, 25, and 30 min at  $\lambda_{ex} = 290$  nm.

Figure S18) solution in 8:2  $H_2O/THF$  is observed, respectively, within 1 min, which went up to 85 and 80% quenching of the emission intensity within 30 min, respectively, at room temperature (Figure 6). These results reveal that aggregates of 3 and 4 are responsive to TNT in solution and the vapor phase.

During the preparation and packaging of explosive devices, nitroaromatics can contaminate the human body, clothing, and



Figure 6. Plot of % quenching of fluorescence of compounds 3 and 4 vs exposure time (min) of TNT vapors.

other materials in the surroundings.<sup>23</sup> In this context, we prepared test strips by dip-coating solutions of aggregates of **3** and **4** in 8:2  $H_2O/THF$  on Whatman filter paper followed by drying the strips under vacuum to test the residual contamination in contact mode.

To signify the vapor-mode test, we also performed a paper strip test in vapor mode by placing a fluorescent paper strip over the top of the glass vial containing solid TNT for 5 min at room temprature. The circular area that was exposed to the TNT vapors was quenched (Figure 7A), which implies the practical sensitivity and applicability of both 3 and 4 toward vapors of TNT.

We performed the paper strip test on both derivatives in contact mode in which fluorescence quenching was observed upon dipping the test strips into a solution of TNT  $(10^{-3} \text{ M})$ (Figure 7B). We also checked the effect of various concentrations of TNT solution on the fluorescent paper strip by applying small spots of different concentrations of TNT to test strips. Dark spots of different strengths were formed, which shows that the regulation of the quenching behavior of TNT is also practically applicable by varying the concentration of TNT even up to  $10^{-12}$  M (Figure 7C). In addition to this, to realize the applications of these carbazolebased derivatives in the solid state, we also studied the response of TNT on the thin solid films of both derivatives on glass plates. For this, we put a drop of the aggregate solution  $(10^{-3})$ M in 8:2 H<sub>2</sub>O/THF) of both derivatives on a glass plate and evaporated the solvent to make thin solid films that are fluorescent in nature. Adding a drop of TNT  $(10^{-5} \text{ M in THF})$ 

to these solid films resulted in abrupt quenching in otherwise visible fluorescence under the excitation of the 365 nm UV lamp (Figure 7D). These results show the practical applicability of derivatives **3** and **4** toward the instant visualization of traces of TNT.

#### EXPERIMENTAL SECTION

**General Information.** All of the UV–vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. All fluorescence spectra were recorded on a Shimadzu RF 5301 PC spectrofluorometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using CDCl<sub>3</sub> as the solvent and TMS as the internal standard. The data are reported as follows: chemical shifts in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet, dd = double doublet, and dt = double triplet), coupling constants (Hz), integration, and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography.

Synthesis of Compound 1-[3-(9-Hexyl)carbazoyl]-3,4-bis(pmethoxyphneyl)-2,5,6-triphenylbenzene (3). A solution of 1a (0.5 g, 1.8 mmol) and 2 (0.816 g, 1.83 mmol) in 1 mL of diphenylether was refluxed for 18 h under an inert atmosphere. Cold methanol (10 mL) was added to the reaction mixture. The methanol layer was decanted off, and the insoluble dark oil was subjected to column chromatography using 3:7 CHCl<sub>3</sub>/hexane as the eluent. The compound was recrystallized from methanol to give 3 as a beige solid. Yield 82%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.79 (t, 3H, J = 4 Hz, CH<sub>3</sub>), 1.18–1.22 (m, 8H, CH<sub>2</sub>), 3.57 (s, 3H, OCH<sub>3</sub>), 3.60 (s, 3H, OCH<sub>3</sub>), 4.12 (t, 2H, J = 4 Hz, NCH<sub>2</sub>), 6.37 (d, 2H, J = 4 Hz, ArH), 6.41 (d, 2H, J = 4 Hz, ArH), 6.62 (d, 2H, J = 4 Hz, ArH), 6.68 (d, 2H, J = 4 Hz, ArH), 6.81–6.82 (m, 6H, ArH), 6.98 (d, 1H, J = 4 Hz, ArH), 7.02-7.12 (m, 5H, ArH), 7.23-7.34 (m, 3H, ArH), 7.61 (s, 1H, ArH), 7.87 (d, 1H, J = 4 Hz, ArH), 7.88 (s, 1H, ArH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  13.94 (CH<sub>3</sub>), 22.50 (CH<sub>2</sub>), 26.91 (CH<sub>2</sub>), 28.89 (CH<sub>2</sub>), 31.51 (CH<sub>2</sub>), 42.51 (NCH<sub>2</sub>), 54.88 (OCH<sub>3</sub>), 107.57 (ArH), 112.21 (ArH), 112.50 (ArH), 118.65 (ArH), 118.85 (ArH), 120.15 (ArH), 121.70 (ArH), 122.38 (ArH), 122.96 (ArH), 125.38 (ArH), 126.02 (ArH), 126.92 (ArH), 127.59 (ArH), 127.99 (ArH), 129.68 (ArH), 129.99 (ArH), 131.71 (ArH), 132.52 (ArH), 132.61 (ArH), 132.64 (ArH), 138.64 (ArH), 139.06 (ArH), 139.72 (ArH), 140.58 (ArH), 140.62 (ArH), 140.91 (ArH), 141.53 (ArH), 142.21 (ArH), 157.04 (ArH), 157.29 (ArH). MS m/z 692:  $[M + 1]^+$  calcd for C<sub>50</sub>H<sub>45</sub>NO<sub>2</sub>: C, 86.80%; H, 6.56%; N, 2.02%; found: C, 86.60%; H, 6.52%; N, 2.00%.

Synthesis of Compound 1-[3-(9-Hexyl)carbazoyl]-3,4-bis(*p*-methoxyphneyl)-2,5-diphenylbenzene (4). A solution of compound 1b (0.35 g, 1.0 mmol) and compound 2 (0.45 g, 1.05 mmol) in 1 mL of diphenylether was refluxed for 18 h under an inert



**Figure 7.** Paper strip test. (A) Vapor-mode detection of TNT (a, c) before and (b, d) after placing the test strips of 3 and 4 over the glass vial containing TNT for 5 min. (B) (a, c) Before and (b, d) after dipping the test strips of 3 and 4, respectively, in the TNT solution  $(10^{-3} \text{ M in THF})$ . (C) Application of small spots of different concentrations of TNT ((i)  $10^{-3}$ , (ii)  $10^{-5}$ , (iii)  $10^{-7}$ , (iv)  $10^{-9}$ , and (v)  $10^{-12}$  M) on test strips of (I) 3 and (II) 4. (D) Change in the fluorescence of 3 and 4 in the solid state in the presence of TNT. (a, c) Thin films of 3 and 4, respectively, (b, d) After adding 1 drop of TNT solution ( $10^{-4}$  M in THF) to the thin film of 3. All images were taken under 365 nm UV illumination.

atmosphere. Cold methanol (10 mL) was added to the reaction mixture. The methanol layer was decanted off, and the insoluble dark oil was subjected to column chromatography using 3:7 CHCl<sub>3</sub>/hexane as the eluent. The compound was recrystallized from methanol to give 4 as a beige solid. Yield 81%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.84 (t,  $3H_1 J = 4 Hz_1 CH_3$ ,  $1.19-1.25 (m, 8H_1 CH_2)$ ,  $3.62 (s, 6H_1 OCH_3)$ , 4.09 (t, 2H, J = 4 Hz, NCH<sub>2</sub>), 6.42 (d, 4H, J = 4 Hz, ArH), 6.70-6.89 (m, 22H, ArH), 7.30-7.36 (m, 2H, ArH), 7.51 (s, 1H, ArH), 7.76 (d, 1H, J = 8 Hz, ArH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 13.96 (CH<sub>3</sub>), 22.49 (CH<sub>2</sub>), 26.77 (CH<sub>2</sub>), 28.71 (CH<sub>2</sub>), 31.46 (CH<sub>2</sub>), 42.84 (NCH<sub>2</sub>), 54.86 (OCH<sub>3</sub>), 106.69 (ArH), 108.42 (ArH), 112.11 (ArH), 118.17 (ArH), 119.92 (ArH), 121.42 (ArH), 123.51 (ArH), 124.86 (ArH), 126.45 (ArH), 126.54 (ArH), 129.42 (ArH), 131.46 (ArH), 131.58 (ArH), 132.44 (ArH), 133.39 (ArH), 140.20 (ArH), 140.72 (ArH), 141.10 (ArH), 156.83 (ArH). MS m/z 768: [M +1]<sup>+</sup> calcd for C56H49NO2; C, 87.58%; H, 6.43%; N, 1.82%; found: C, 87.42%; H, 6.40%; N, 1.80%.

#### CONCLUSIONS

We designed and synthesized AIEE-active derivatives **3** and **4**. Both derivatives form fluorescent organic aggregates in mixed aqueous media and the aggregates work as efficient, selective fluorescent sensors for the nanomolar detection of TNT in solution, solid, and vapor, which enhances the scope of materialization of the TNT probes.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Fluorescence, UV-vis, NMR, and mass spectra of compounds 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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#### ABBREVIATIONS

AIEE = aggregation-induced emission enhancement

#### REFERENCES

(1) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Chem. Soc. Rev. 2011, 40, 5361.

(2) Toxicological profile for 2,4,6-trinitrotoluene, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

(3) (a) Goldman, E. R.; Medintz, I. L.; Whitley, J. L.; Hayhurst, A.; Clapp, A. R.; Uyeda, H. T.; Deschamps, J. R.; Lassman, M. E.; Mattoussi, H. J. Am. Chem. Soc. 2005, 127, 6744. (b) Zhang, K.; Zhou, H.; Mei, Q.; Wang, S.; Guan, G.; Liu, R.; Zhang, J.; Zhang, Z. J. Am. Chem. Soc. 2011, 133, 8424.

(4) Qu, W. G.; Deng, B.; Zhong, S. L.; Shi, H. Y.; Wang, S. S.; Xu, A. W. Chem. Commun. 2011, 47, 1237.

(5) Yang, L. B.; Chen, G. Y.; Wang, J.; Wang, T. T.; Li, M. Q.; Liu, J. H. *J. Mater. Chem.* **2009**, *19*, 6849.

(6) (a) Riskin, M.; Vered, R. T.; Bourenko, T.; Granot, E.; Willner, I. J. Am. Chem. Soc. 2008, 130, 9726. (b) Riskin, M.; Tel-Vered, R.; Lioubashevski, O.; Willner, I. J. Am. Chem. Soc. 2009, 131, 7368. (c) Frasconi, M.; Tel-Vered, R.; Riskin, M.; Willner, I. J. Am. Chem. Soc. 2010, 132, 9373.

(7) (a) Apodaca, D. C.; Pernites, R. B.; Mundo, F. R. D.; Advincula, R. C. Langmuir 2011, 27, 6768. (b) Thomas, S. W.; Joly, G. D.; Swager, T. M. Chem. Rev. 2007, 107, 1339. (c) Narayanan, A.; Varnavski, O. P.; Swager, T. M.; Goodson, T. J. Phys. Chem. C 2008, 112, 881. (d) Che, Y.; Yang, X.; Liu, G.; Yu, C.; Ji, H.; Zuo, J.; Zhao, J.; Zang, L. J. Am. Chem. Soc. 2010, 132, 5743. (e) Wang, X.; Guo, Y.; Li, D.; Chen, H.; Sun, R.-c. Chem. Commun. 2012, 48, 5569. (f) Shanmugaraju, S.; Joshi, S. A.; Mukherjee, P. S. J. Mater. Chem. 2011, 21, 9130. (g) Sanchez, J. C.; Trogler, W. C. J. Mater. Chem. 2008, 3143.

(8) (a) Kartha, K. K.; Babu, S. S.; Srinivasan, S.; Ajayaghosh, A. J. Am. Chem. Soc. 2012, 134, 4834. (b) Naddo, T.; Che, Y.; Zang, W.; Balakrishnan, K.; Yang, X.; Yen, M.; Zhao, J.; Moore, J. S.; Zhang, L. J. Am. Chem. Soc. 2007, 129, 6978. (c) Zang, L.; Che, Y.; Moore, J. S. Acc. Chem. Res. 2008, 41, 1596. (d) Zhang, C.; Che, Y.; Yang, X.; Bunes, B. R.; Zang, L. Chem. Commun. 2010, 46, 5560.

(9) (a) Lee, Y. H.; Liu, H.; Lee, J. Y.; Kim, S. H.; Kim, S. K.; Sessler, J. L.; Kim, Y.; Kim, J. S. *Chem.—Eur. J.* **2010**, *16*, 5895. (b) Howard, P. H., Meylan, W. M., Eds. Handbook of Physical Properties of Organic Chemicals; CRC Press: Boca Raton, FL, 1997. (c) Pushkarsky, M. B.; Dunayevskiy, I. G.; Prasanna, M.; Tsekoun, A. G.; Go, R.; Kumar, C.; Patel, N. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 19630.

(10) (a) Wang, J.; Mei, J.; Yuan, W.; Lu, P.; Qin, A.; Sun, J.; Ma, Y.; Tang, B. Z. J. Mater. Chem. **2011**, 21, 4056. (b) Liu, J.; Zhing, Y.; Lu, P.; Hong, Y.; Lam, J. W. Y.; Faisal, M.; Yu, Y.; Wong, K. S.; Tang, B. Z. Polym. Chem. **2010**, 1, 426. (c) Lu, P.; Lam, J. W. Y.; Jim, C. K. W.; Yuan, W.; Xie, N.; Zhong, Y.; Hu, Q.; Wong, K. S.; Cheuk, K. K. L.; Tang, B. Z. Macromol. Rapid Commun. **2010**, 31, 834.

(11) Comparison of aggregates of **3** and **4** with previous reports with respect to selectivity towards TNT,  $K_{SV}$  values, and phase of experimentation are given in the Supporting Information, Table 1.

(12) Wu, W.; Qiu, G.; Yu, G.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 1977.

(13) Thomas, K. R. J.; Velusamy, M.; Lin, J. T.; Sun, S. S.; Tao, Y. T.; Chuen, C. H. *Chem. Commun.* **2004**, 2328.

(14) Walsh, C. J.; Mandal, B. K. J. Org. Chem. 1999, 64, 6102.

- (15) Tang, B. Z.; Geng, Y.; Lam, J. W. Y.; Li, B.; Jing, X.; Wang, X.;
- Wang, F.; Pakhomov, A.; Zhang, X. X. Chem. Mater. 1999, 11, 1581.
- (16) Demas, J. N.; Grosby, G. A. J. Phys. Chem. 1971, 75, 991.

(17) Dong, S.; Li, Z.; Qin, J. J. Phys. Chem. B 2009, 113, 434.

(18) Haidekker, M. A.; Theodorakis, E. A. Org. Biomol. Chem. 2007, 5, 1669.

(19) Ishihara, S.; Furuki, Y.; Takeoka, S. Polym. Adv. Technol. 2008, 19, 1097.

(20) Olley, D. A.; Wren, E. J.; Vamvounis, G.; Fernee, M. J.; Wang,

X.; Burn, P. L.; Meredith, P.; Shaw, P. E. Chem. Mater. 2011, 23, 789.
(21) Ding, L.; Liu, Y.; Cao, Y.; Wang, L.; Xin, Y.; Fang, Y. J. Mater. Chem. 2012, 22, 11574.

(22) Sohn, H.; Sailor, M. J.; Magde, D.; Trogler, W. C. J. Am. Chem. Soc. 2003, 125, 3821.

(23) (a) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.;
Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* 2000, 100, 2595.
(b) Kim, T. H.; Lee, B. Y.; Jaworski, J.; Yokoyama, K.; Chung, W.-J.;
Wang, E.; Hong, S.; Majumdar, A.; Lee, S.-W. ACS Nano 2011, 5, 2824.