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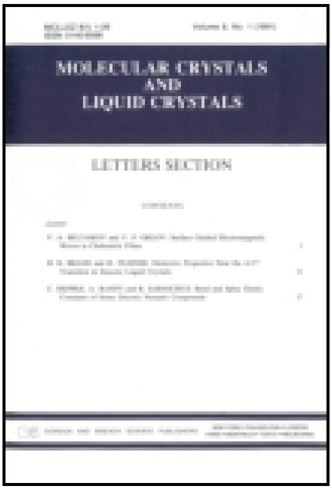

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PL Quenching of Poly(3-hexylthiophene) by 2,2′,7,7′-Tetradiphenylamino-9,9′-Bifluorenylidene

On You Park[a], Hee Un Kim[a] & Do-Hoon Hwang[a]
[a] Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan, Republic of Korea

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PL Quenching of Poly(3-hexylthiophene) by 2,2′,7,7′-Tetradiphenylamino-9,9′-Bifluorenylidene

ON YOU PARK, HEE UN KIM,
AND DO-HOON HWANG*

Department of Chemistry and Chemistry Institute for Functional Materials,
Pusan National University, Busan, Republic of Korea

2,2′,7,7′-Tetradiphenylamino-9,9′-bifluorenylidene, TDPABF, was synthesized by reductive dimerization using Lawesson's reagent. It is soluble in common organic solvents such as dichloromethane, chloroform, and 1,2-dichlorobenzene. Its synthesis was confirmed by ^{1}H-, ^{13}C- *NMR, MALDI-TOF, and FT-IR spectroscopy. Its HOMO and LUMO energy levels were –5.33 eV and –2.98 eV, respectively, using photoelectron spectroscopy and UV-Vis absorption spectra. Its fluorescence quenching properties were investigated through a Stern-Volmer quenching experiment. The PL intensity significantly decreased on increasing the concentration of TDPABF in a P3HT chloroform solution. The calculated Stern-Volmer quenching constant was* $9.1 \times 10^{4}\ M^{-1}$*, which is higher than that reported for* $PC_{61}BM$.

Keywords 9,9′-bifluorenylidene derivative; electron acceptor; photoluminescence quenching

1. Introduction

Recently, organic photovoltaic devices (OPVs) that use organic p-type (donor) and n-type (acceptor) semiconductors have been extensively studied as alternate energy sources because of their many advantages over silicon-based inorganic solar cells, such as simple device structure, easy fabrication, lightweight, and low production cost [1–3]. Fullerene derivatives have been widely used as electron-accepting materials for OPVs because they have high electron mobility and suitable lowest unoccupied molecular orbital (LUMO) energy levels that can be tuned through molecular engineering [4–7].

However, fullerene derivatives also have some drawbacks as electron acceptors in OPVs, such as weak light absorption in the UV-visible region, difficult synthetic and purification processes, and high production cost [8]. Moreover, chemical modification of fullerene derivatives is limited to several addition reactions. Therefore, the development of new electron-accepting materials is very important in order to overcome the drawbacks of fullerene derivatives.

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*Address correspondence to Prof. Do-Hoon Hwang, Department of Chemistry, Pusan National University, Busan 609-735, Korea. Tel.: +82-51-510-2232; Fax: +82-51-516-7421. E-mail: dohoonhwang@pusan.ac.kr

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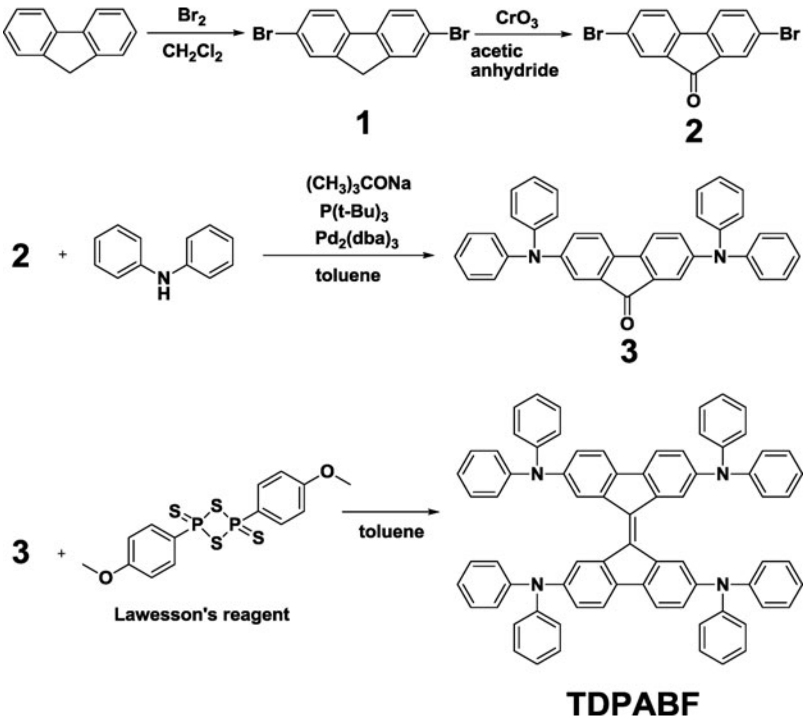
Several non-fullerene–type electron acceptors have been reported for OPVs, such as molecules and polymers containing benzothiadiazole [8], diketopyrrolopyrrole (DPP) [9], or 9,9′-bifluorenylidene (99′BF) [10] derivatives. Among these, 99′BF derivatives have attracted the most scientific interest because of their unique electron-accepting properties. Wudl et al. suggested that, in the ground state, 99′BF is forced to adopt a coplanar structure because of steric repulsion between H1-H1′ and H8-H8′. The addition of one electron could break the double bond, enabling the two fluorenes to easily tilt. Also, one of the fluorene units could have a 14-π-electron system, which fulfills Hückel's requirement for aromacity [10]. Accordingly, 99′BF has a high electron affinity, and therefore, easily accepts electrons from donor polymers in OPVs.

In this paper, we describe the design and synthesis of a new 99′BF derivative, i.e., 2,2′,7,7′-tetradiphenylamino-9,9′-bifluorenylidene (TDPABF), as an electron-accepting molecule. Four diphenylamine groups were introduced to 99′BF to raise the LUMO energy level. We also characterized the optical and electrochemical properties and performed a Stern-Volmer quenching experiment with P3HT to evaluate the effectiveness of TDPABF as an electron acceptor for OPVs. The synthetic route to TDPABF is shown in Scheme 1.



Scheme 1. Synthetic route for 2,2′,7,7′-tetra(diphenylamino)-9,9′-bifluorenylidene (TDPABF).

2. Experimental

2.1 Materials

Fluorene and Lawesson's reagent were purchased from Alfa Aesar, and chromium oxide, diphenylamine, sodium (tert-butoxide), and tris(tert-butyl) phosphine were purchased from Aldrich. Tris(dibenzylidene acetone) dipalladium(0) was purchased from Strem Chemicals, Inc. All chemicals were used as received without further purification.

2.2 Material Synthesis

2,7-Dibromo-9H-fluorene (1) and 2,7-dibromo-9H-fluoren-9-one (2) were prepared according to previously reported syntheses [11].

2.2.1 Synthesis of 2,7-bis(diphenylamino)-9H-fluoren-9-one (3). A prepared catalyst solution of tris(dibenzylidene acetone)dipalladium(0) (0.2 g, 0.2 mmol) and tris(tert-butyl) phosphine (0.04 g, 0.2 mmol) in toluene was added to a solution of **2** (3.0 g, 8.9 mmol), diphenylamine (3.3 g, 19.5 mmol), and sodium (tert-butoxide) (2.0 g, 20.4 mmol) in toluene (150 mL); the mixture was refluxed at ∼110 °C under a nitrogen atmosphere for one day. Crude product was obtained after cooling, extraction with ethyl acetate, and the usual work-up. The crude product was purified by column chromatography (dichloromethane/hexane = 1:3) to give the desired product (3.9 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$; δ [ppm]): 7.34 (s, 2H), 7.24–7.30 (m, 10H), 7.03–7.14 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$; δ [ppm]): 193.68, 148.54, 147.41, 138.36, 136.06, 129.71, 128.89, 124.84, 123.70, 120.64, 119.72. FT-IR (KBr, cm^{-1}): 3036 (multi, aromatic C—H stretches), 1711 (single, C═O), 1589, 1493 (single, aromatic C═C).

2.2.2 Synthesis of 2,2′,7,7′-tetra(diphenylamino)-9,9′-bifluorenylidene (TDPABF). A mixture of compound **3** (3.0 g, 5.8 mmol) and Lawesson's reagent (1.7 g, 4.1 mmol) in toluene (70 mL) was heated at reflux for 12 h. Crude product was obtained after cooling, extraction with ethyl acetate, and the usual work-up. The crude product was purified by column chromatography (dichloromethane/hexane = 1:6) to give the desired product (1.2 g, 21%). ^{1}H NMR (300 MHz, $CDCl_3$; δ [ppm]): 8.07 (s, 4H), 7.40 (d, 4H), 7.17 (t, 16H), 6.91–6.96 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$; δ [ppm]): 147.92, 146.56, 141.82, 139.70, 136.74, 129.46, 127.75, 124.15, 123.75, 122.50, 120.35. FT-IR (KBr, cm^{-1}): 3032 (multi, aromatic C–H stretches), 1589, 1493 (single, aromatic C═C). MALDI-TOF (m/z = 996.49 (M+)). Elemental analysis for $C_{74}H_{52}N_4$: calculated, C: 89.13, H: 5.26, N: 5.62; found, C: 88.58, H: 5.16, N: 6.02.

2.3 Measurements

^{1}H and ^{13}C NMR spectra were recorded using a Varian 300 spectrometer, and Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet 380 spectrometer. Thermals analysis was performed on a Q600 under a nitrogen atmosphere at a heating and cooling rate of 10°C/min. The MALDI-TOF mass spectra were recorded using a Voyager DE-STR mass spectrometer (Applied Biosystems). The absorption and photoluminescence spectra were recorded using a Shimadzu UV-3600 spectrometer and Shimadzu RF 5301 PC fluorometer, respectively. The photoelectron spectra were measured using an AC-2 (Hitachi High Tech) spectrometer.

3. Result and Discussion

3.1 Characterization

TDPABF was synthesized via reductive coupling of 2,7-bis(diphenylamino)-9H-fluoren-9-one using Lawesson's reagent, as shown in Scheme 1. Figures 1 show the ^{1}H NMR spectra of TDPABF. The aromatic protons in TDPABF appear between 8.07 and 6.91 ppm. The signal for the four protons that are nearest to the core double bond (H_c) is shifted furthest downfield and appears at 8.07 ppm as a singlet. The four protons in the fluorene ring (H_a)

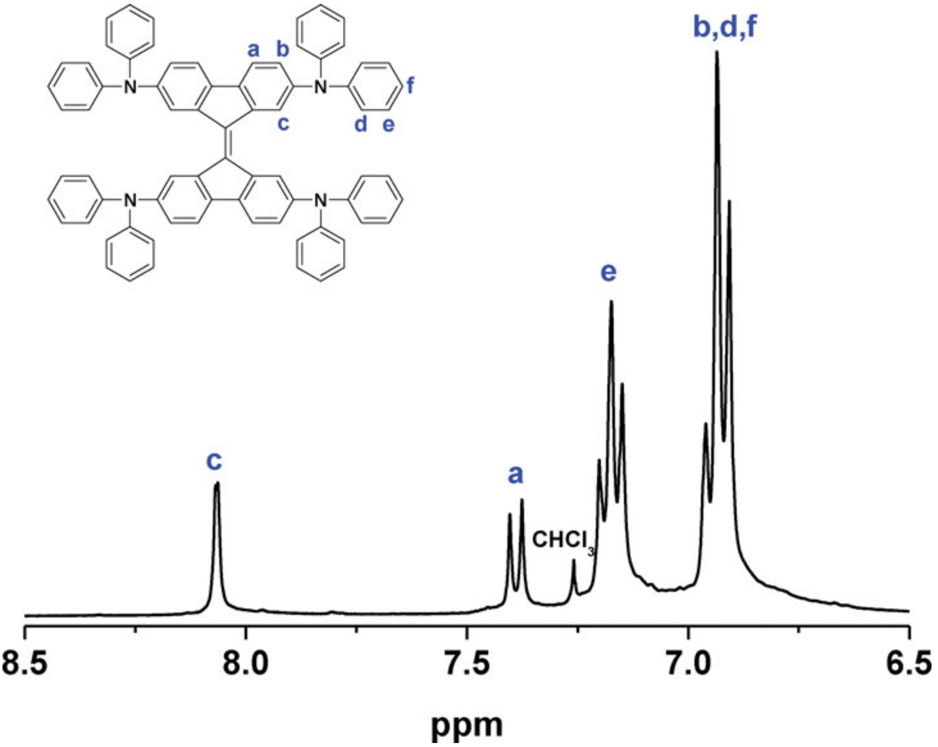


Figure 1. ^{1}H NMR spectra of TDPABF.

correspond with the doublet at 7.40 ppm, while the sixteen protons in the diphenylamine group (H_e) are evident at 7.17 ppm as a triplet. The remaining aromatic proton signals overlap between 6.91 and 6.96 ppm.

The FT-IR spectra of **3** and TDPABF are shown in Figure 2. The spectra feature aromatic C–H stretching at 3036 and 3032 cm^{-1}, respectively, and aromatic C$=$C stretching at 1589 and 1493 cm^{-1}, respectively. The spectrum of **3** shows a strong carbonyl absorption peak at 1711 cm^{-1}, whereas the carbonyl peak is completely absent in the spectrum of TDPABF. The absorption peak corresponding to the core double bond was not observed because the symmetrically substituted double bond is inactive in FT-IR spectroscopy.

The thermal stability of TDPABF was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. TDPABF showed good thermal stability, losing <5% of its weight upon heating up to 400°C. This value is similar to that for PC$_{61}$BM and other fullerene derivatives [12]. The melting point of TDPABF is 162.3°C, as determined by differential scanning calorimetry (DSC). The TGA and DSC thermograms of TDPABF are shown in Figure 3.

3.2 Simulation of Molecular Structure

To elucidate the three-dimensional shapes of the molecules and the electron distributions in the highest occupied molecular orbital (HOMO) and LUMO energy levels of TDPABF, density functional theory (DFT) calculations were performed on a model compound using DMol 3 software [13, 14]. Figure 4 shows the three-dimensional shapes of TDPABF and the electron distribution of the HOMO and LUMO energy levels. The dihedral angle (θ)

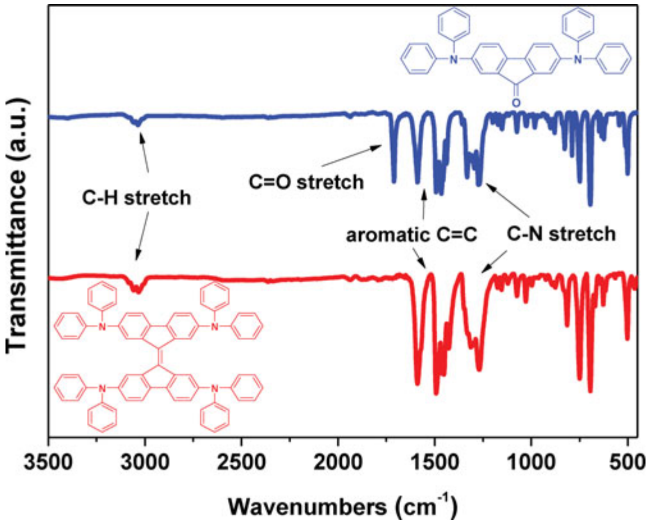


Figure 2. FT-IR spectra of 3 and TDPABF.

between the two core fluorene units that are attached by a double bond is 40.4° because of the steric interaction of the bulky diphenylamine groups. The electrons in the HOMO energy level are distributed on one side of the fluorene and diphenylamine units, whereas they are mainly distributed on the core double bond and fluorene units in the LUMO energy level.

3.3 *Optical and Electrochemical Properties*

Figure 5 shows the UV-visible absorption spectra of TDPABF in chloroform solution and as a solid thin film. The absorption spectrum of the chloroform solution shows four main absorption bands at approximately 306, 319, 375, and 462 nm; the absorption peaks

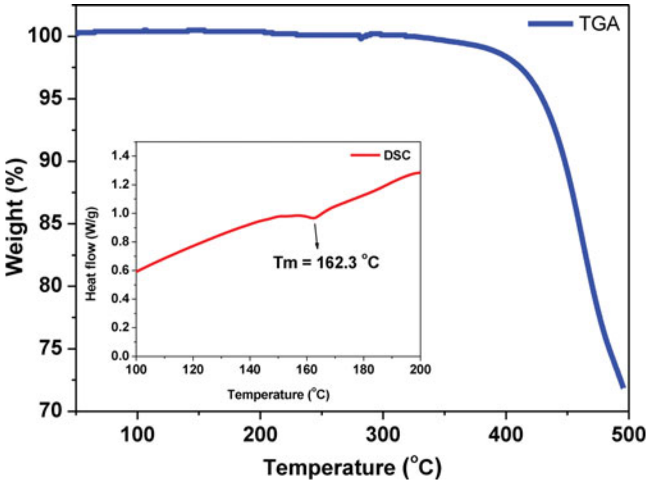


Figure 3. TGA and DSC thermograms of TDPABF.

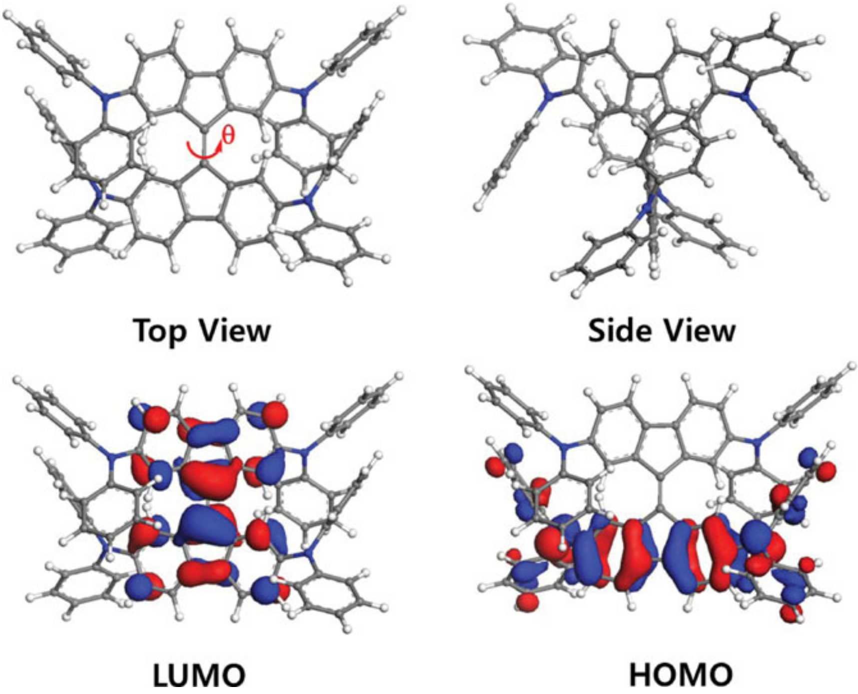


Figure 4. Three-dimensional shape of TDPABF and electron distribution of the HOMO and LUMO energy levels.

in the ultraviolet region correspond to the π-π^* transitions of the diphenylamine and fluorene units, and the absorption band at 462 nm corresponds to the π-π^* transition of the 99′BF structure. The latter absorption band of TDPABF is slightly red-shifted from that previously reported for 99′BF (458 nm) [10] because of the longer effective conjugation

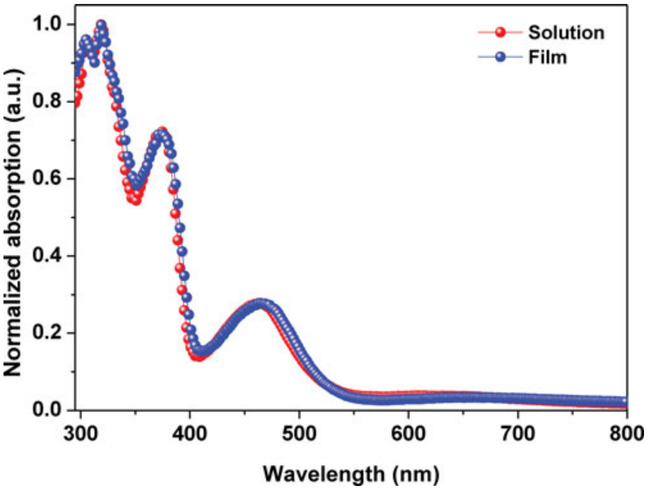


Figure 5. UV-vis spectra of TDPABF in chloroform solution and as a solid thin film.

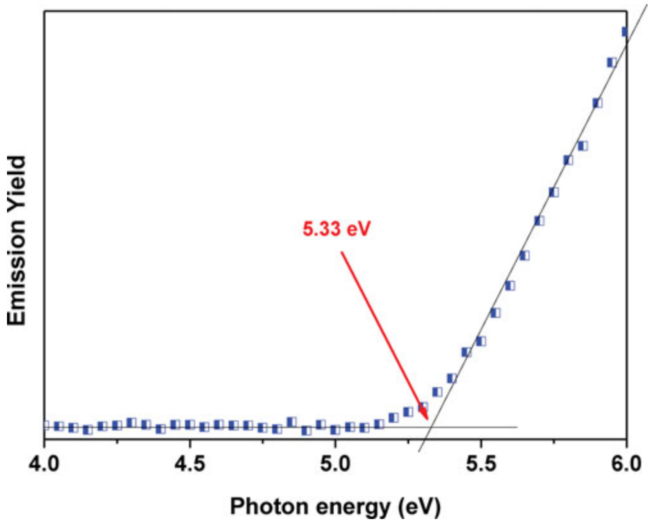


Figure 6. Photoelectron spectra of TDPABF.

of TDPABF due to the incorporation of the diphenylamine groups. Interestingly, the UV-visible absorption spectra of TDPABF in solution and as a solid thin film state were very similar, which is consistent with the simulated structure of TDPABF, because the tilted-core structure likely impairs effective packing of the molecule in the solid state. The maximum absorption (λ_{max}) and edge wavelengths (λ_{onset}) of the TDPABF solid thin film state were 466 and 528 nm, respectively. The optical band gap energy (E_g^{opt}) of the TDPABF solid thin film was determined to be 2.35 eV from its onset absorption wavelength (λ_{onset}). The measured optical band gap of TDPABF is slightly smaller than that reported for 99′BF (~2.42 eV) because of the introduction of electron-donating diphenylamine moieties.

The HOMO energy level of the TDPABF solid thin film was determined using photoelectron spectroscopy. The measured ionization potential of TDPABF was −5.33 eV, as shown in Figure 6. The LUMO energy level of TDPABF was determined to be −2.98 eV by adding the measured optical band gap and HOMO energy level (i.e., $E_{LUMO} = E_{HOMO} + E_g^{opt}$). The LUMO energy level of TDPABF is much higher than that reported for 99′BF (−3.37 eV), which was measured by cyclic voltammetry, possibly because of the increased electron density in TDPABF owing to the incorporation of the electron-donating diphenylamine groups. Therefore, the electron-donating diphenylamine groups raise the LUMO energy level of TDPABF relative to that of 99′BF.

To evaluate the electron-accepting ability of TDPABF, we investigated the fluorescence quenching of poly(3-hexylthiophene) (P3HT) by TDPABF. The photoluminescence (PL) intensities of P3HT solutions were measured with different mole ratios of TDPABF. At low concentrations of fluorescence quencher, relationship between the fluorescence intensity and concentration of quencher can be expressed by Stern-Volmer equation as follows:

$$\Phi^{\circ}\big/\Phi = 1 + K_{sv}[\text{quencher}],$$

where Φ^{o} and Φ represent the PL intensity in the absence and presence of the quencher, respectively, and K_{sv} is the Stern-Volmer quenching constant. The obtained Stern-Volmer plot for TDPABF is shown in Figure 7. The plot is linear in the quencher concentration

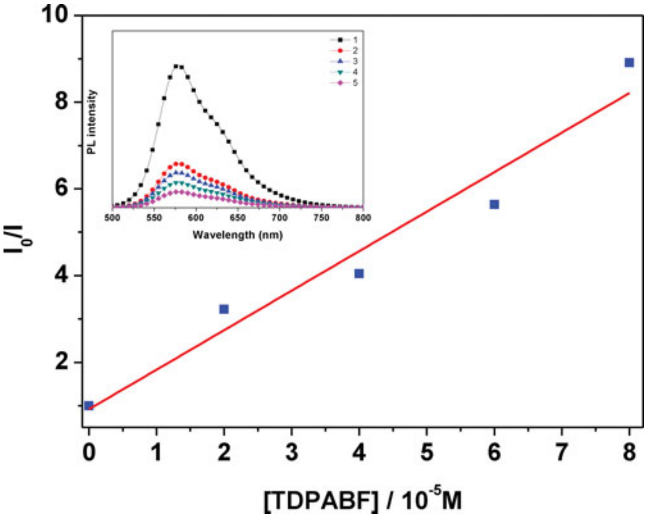


Figure 7. PL-quenching spectra of P3HT:TDPABF in chloroform solution with increasing concentration of TDPABF are shown in the inset: (1) 0.0 M, (2) 2.0 × 10^{-5} M, (3) 4.0 × 10^{-5} M, (4) 6.0 × 10^{-5} M, (5) 8.0 × 10^{-5} M.

range 0–8.0 × 10^{-5} M. The PL intensity of P3HT dramatically decreased after the addition of TDPABF. The obtained K_{sv} value was 9.1 × 10^4 M^{-1}, which is higher than that reported for $PC_{61}BM$ (2.4 × 10^3 M^{-1}) with P3HT as the fluorophore [15]. The high K_{sv} value of TDPABF indicates that it has a higher binding affinity for P3HT than $PC_{61}BM$. The PL quenching experiment and high K_{sv} value suggest that TDPABF efficiently accepts electrons from the P3HT donor polymer. TDPABF is expected to be used as a new electron acceptor in organic photovoltaic cells. The fabrication of OPVs using TDPABF is currently being investigated.

4. Conclusions

We designed and synthesized TDPABF as a non-fullerene–type electron acceptor. The synthesis of TDPABF was confirmed using ^{1}H NMR, ^{13}C NMR, MALDI-TOF, and FT-IR spectroscopy. TDPABF showed a broader absorption spectrum than fullerene derivatives and exhibited a good fluorescence-quenching ability with a relatively high Stern-Volmer quenching constant. We expect that TDPABF will be applied as a new n-type electron acceptor in organic photovoltaic cells.

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