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Terpyridine-based donor–acceptor metallo-supramolecular polymers with tunable band gaps: Synthesis and characterization

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ABSTRACT

Three new building blocks containing the electron-donor fused-ring motifs carbazole, dithienosilole (DTS) and dithienopyrrole (DTP) and the 2,2′:6′,2″-terpyridine electron-acceptor motif were designed and synthesized. Directed by transition metal ions, the self-assembly of the building blocks triggered polymerization to form the corresponding metallo-supramolecular polymers **PCzTPY**, **PSiTPY** and **PNTPY**, respectively. The UV–vis absorption maxima of the building blocks occur at long wavelengths (351, 368 and 430 nm for **CzTPY**, **SiTPY** and **NTPY**, respectively), which arises from intramolecular charge transfer (ICT) transitions. However, the absorption maxima of their corresponding metallo-supramolecular polymers are clearly red-shifted (to 394, 431 and 509 nm for **PCzTPY**, **PSiTPY** and **PNTPY**, respectively), which is caused by the incorporation of the transition metal ion into the backbones of the target polymers. Based on the above strategies, the resulting metallo-polymers exhibit reduced energy gaps, which are 2.07, 1.97 and 1.56 eV for the **PCzTPY**, **PSiTPY** and **PNTPY** metallo-supramolecular polymers, respectively.

1. Introduction

Over the past few decades, the design and study of π-conjugated organic semiconductors has attracted increasing attention. One of the important advantages of organic/polymer semiconductor materials is that the levels of their frontier orbitals and energy gaps of the organic and polymer molecules can be tuned easily by molecular design; consequently, the resulting photoelectronic and electrochemical properties can be finely tailored. Presently, conjugated polymers with alternating electron-donating (D) and electron-accepting (A) units along the same backbone have become especially useful in optoelectronics, such as OLEDs [1], photovoltaic devices [2], chemical sensors [3], field-effect transistors (FETs) [4], and NLOs [5]. Such donor–acceptor organic/polymers exhibit narrow energy gaps and strong dipoles resulting from intramolecular charge transfer (ICT). Further, these molecules possess the ability to span the optical absorption spectrum across the visible and near-IR range. The strength, nature and type of the donor and acceptor motifs heavily influence the energy levels of the frontier orbitals; hence, the optical and electronic properties of the organic light-emitting, light-absorbing and semiconducting materials. Although many studies exist concerning the synthesis, properties and the relationship between structure and properties, many phenomena in such push–pull systems of D/A materials have not been sufficiently clarified, and a broad understanding of the electronic and photophysical properties and energetic alignment of the frontier orbitals remains unclear.

Electron-rich units such as triphenylamines [6], carbazole [7], benzodithiophene [8], dithieno[3,2-b:2′,3′-d]silole (DTS) [9–11], and dithieno[3,2-b:2′,3′-d]pyrrole (DTP) [12–15] and their derivatives have been developed as donor units in D/A polymer materials. One approach to their synthetic modification is to introduce fused aromatic units into the conjugated backbone, which results in materials that exhibit enhanced carrier mobilities, delocalized π-conjugated organic and polymer semiconductors and reduced

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energy gaps. Among the electron-rich units, carbazole, dithieno[3,2-b:2′,3′-d]silole (DTS) and dithieno[3,2-b:2′,3′-d]pyrrole (DTP) contain fused planar tricyclic systems and possess low-lying LUMO energy levels and enhanced carrier mobilities. Further, because of their good molecular planarity and their capacity to be easily modified, the introduction of these fused-ring donor motifs into various π-conjugated polymeric and molecular materials is desirable for providing high carrier mobilities, enhanced fluorescence and reduced band gaps [16–18].

2,2′:6′,2″-Terpyridine and its derivatives are well-studied, though they remain fascinating because of their outstanding favorable geometry and because they can be used in metallomacrocycles [19], terpyridine-ruthenium(II) complexes for their photovoltaic performance [20], and supramolecular materials and chemistry [21–23]. Interest in supramolecular polymers (SP), in which the monomeric building blocks are held together via non-covalent interactions, such as hydrogen bonding, metal coordination, electrostatic interactions, hydrophobic interactions and $\pi-\pi$ interactions, has been stimulated because of the vast of progresses in modern supramolecular chemistry [24]. The so-called metallo-supramolecular polymers, which are based on metal-ligand coordination, have recently made rapid progress in supramolecular systems and materials [25,26]. The introduction of metal ions into the backbones of the supramolecular polymers results in some very interesting photophysical and electrochemical properties. At the same time, pyridine rings, especially terpyridine, can be used as the electron-withdrawing units, and monomeric building blocks incorporated with 2,2′:6′,2″-terpyridine can be used to generate D-A π-conjugated organic/polymers materials [27,28].

Based on the above considerations, we report herein the details of the synthesis of novel building blocks based on π-conjugated 2,2′:6′,2″-terpyridine. Using Suzuki coupling reactions with Pd-catalysts, the electron-acceptor π-conjugated 2,2′:6′,2″-terpyridine was coupled with the electron-donor moieties carbazole, DTS and DTP, which have good molecular planarity because of their fused-rings, to synthesize the monomeric building blocks **CzTPY**, **SiTPY** and **NTPY**, respectively (Scheme 1). Directed by the transition metal ion Zn^{2+}, three new donor–acceptor metallo-supramolecular polymers were synthesized *via* self-assembly polymerization under moderate conditions (Scheme 2). The effects of the D-A molecular structures and the transition metal ions on the photophysical, electrochemical properties and the energy gaps of the resulting metallo-polymers were fully investigated in this paper.

2. Experimental section

2.1. Synthesis of the monomeric building blocks and metallo-supramolecular polymers

2.1.1. 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**1**)

To a solution of 2,2′-bithiophene (2.78 g, 16.7 mmol) in the mixed solvent of glacial acetic acid (20 mL) and $CHCl_3$ (23 mL) at 0 °C was added dropwise bromine (9.8 g, 61.3 mmol) in 20 mL $CHCl_3$. The mixture was stirred at room temperature overnight and then heated under reflux for 24 h. After cooling to room temperature, 50 mL of 10% KOH aqueous solution was added, followed by extraction with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed by evaporation. After recrystallization from ethanol, colorless crystals were obtained (7.50 g, 93%). ^1H NMR ($CDCl_3$), δ (ppm): 7.04 (s, 2H).

2.1.2. 3,3′-dibromo-2,2′-bithiophene (**2**)

Compound **1** (25.00 g, 51.8 mmol) was added to a refluxing dispersion of zinc powder (13.00 g, 0.3 mol) in a mixing solution of 150 mL ethanol, 30 mL water, 60 mL glacial acetic acid and 5 mL 3 M HCl. After refluxing for an additional 6 h and then cooling to room temperature, the mixture was filtered and washed three times with ethanol. The solvent was then removed by evaporation and water was added. The mixture was then extracted with diethyl ether and then dried over anhydrous $MgSO_4$. The solvent was removed by evaporation, and the crude product was recrystallized in hexane to afford colorless crystals (14.54 g, 86.3%). ^1H NMR ($CDCl_3$), δ (ppm): 7.41 (d, J = 5.5 Hz, 2H), 7.09 (d, J = 5.0 Hz, 2H).

2.1.3. N-dodecyldithieno[3,2-b:2′,3′-d]pyrrole (**3**)

A mixture of **2** (7.50 g, 23.3 mmol), NaO^{t}Bu (5.38 g, 56.0 mmol) and BINAP (1.45 g, 2.2 mmol) in 65 mL dry toluene was purged with N_2 for 30 min. A catalytic amount of Pd_2dba_3 and dodecylamine (4.54 g, 24.5 mmol) were added to the above mixture and the reaction mixture was stirred and heated under reflux overnight. After cooling to room temperature, water was added to the mixture. The mixture was extracted with diethyl ether and then dried over anhydrous $MgSO_4$. The solvent was removed by evaporation. The crude product was purified by silica gel column chromatography (hexane) to give the product as a light yellow oil (6.69 g, 82.6%). ^1H NMR ($CDCl_3$), δ (ppm): 7.13 (d, J = 5.0 Hz, 2H), 7.00 (d, J = 5.5 Hz, 2H), 4.20 (t, J = 7.0 Hz, 2H), 1.86 (m, 2H), 1.30–1.24 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H).

2.1.4. 2,6-Dibromo-N-dodecyldithieno[3,2-b:2′,3′-d]pyrrole (**4**)

To a solution of **3** (3.15 g, 9.1 mmol) in 300 mL THF was added NBS (3.23 g, 18.1 mmol) at 0 °C. Water was added after the solution was stirred for 2 h. The mixture was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was recrystallized from CH_2Cl_2/methanol to give light yellow crystals (3.71 g, 81.2%). ^1H NMR ($CDCl_3$), δ (ppm): 6.91 (s, 2H), 4.08 (t, J = 7.0 Hz, 2H), 1.80 (m, 2H), 1.28–1.24 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H).

2.1.5. 3,3′-dihexylsilylene-2,2′-bithiophene (**5**)

2.2 M n-BuLi in hexane (7.32 mL, 16.2 mmol) was added dropwise to a solution of **2** (2.49 g, 7.7 mmol) in anhydrous THF (55 mL) under vigorous stirring at −78 °C. The mixture was then stirred at −78 °C for 1 h. Then, a solution of dichlorodihexylsilane (2.50 mL, 8.1 mmol) in THF (100 mL) was added dropwise. The reaction mixture was stirred at −78 °C for an additional 5 h. The mixture was allowed to warm to room temperature overnight with stirring. The reaction mixture was quenched and a saturated aqueous NH_4Cl solution was added. The mixture was extracted with diethyl ether and then dried over $MgSO_4$. The solvent was removed by evaporation, and the crude product was purified by silica gel column chromatography (hexane) to yield a light yellow liquid (1.84 g, 66.6%). ^1H NMR ($CDCl_3$), δ (ppm): 7.19 (d, J = 4.5 Hz, 2H), 7.05 (d, J = 4.5 Hz, 2H), 1.41–0.85 (m, 26H).

2.1.6. 5,5′-dibromo-3,3′-dihexylsilylene-2,2′-bithiophene (**6**)

To a solution of **5** (0.26 g, 0.7 mmol) in 10 mL DMF was added NBS (0.28 g, 1.6 mmol) in one portion. The mixture was stirred at room temperature for 10 min, and then water was added. The mixture was extracted with diethyl ether. The combined organic phase was washed with water and dried over $MgSO_4$. The solvent was removed, and the product was purified by silica gel column chromatography (hexane) to afford a green liquid (0.31 g, 89.1%). ^1H NMR ($CDCl_3$), δ (ppm): 6.99 (s, 2H), 1.34–0.88 (m, 26H).

2.1.7. 2,7-Dibromo-N-octylcarbazole (**7**)

To a solution of 2,7-dibromocarbazole (1.63 g, 50.0 mmol) in 10 mL DMSO were added 1-bromooctane (1.45 g, 75.0 mmol) and 5 mL of a 50% NaOH solution. The mixture was stirred at room