



Synthesis of metal-free organic dyes containing tris(dodecyloxy)phenyl and dithienothiophenyl units and a study of their mesomorphic and photovoltaic properties



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ABSTRACT

In this study we synthesized three metal-free organic dyes (**Cpd11**, **Cpd16**, and **Cpd22**) featuring 3,4,5-tris(dodecyloxy)phenyl and cyanoacrylic acid moieties as electron-donor and electron-acceptor/anchoring units, respectively, linked through various dithienothiophenyl conjugated spacers. **Cpd16** exhibits mesomorphic properties, confirmed through polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction (XRD), due to the appropriate ratio of the lengths of its flexible chain to its rigid core. Molecular modeling of **Cpd16**, and its *d*-spacing determined from XRD data, verified the existence of a tilt angle in the SmC phase. Among these metal-free organic dyes, a dye-sensitized solar cell incorporating **Cpd16** exhibited the best performance, presumably because of its better packing and its mesomorphic properties; the power conversion efficiency was 3.72% ($V_{oc}=0.58$ V; $J_{sc}=9.98$ mA cm⁻²; $FF=0.65$) under simulated AM 1.5 irradiation (100 mW cm⁻²).

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1. Introduction

The development of novel materials for use in organic optoelectronic devices, such as dye-sensitized solar cells (DSSCs),¹ has become a popular research topic in the quest for low-cost, green materials for sustainable use and a decrease in demand for fossil fuels and nuclear power. DSSCs based on Ru-photosensitizers,^{2,3} such as *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (**N3**)⁴ and related derivatives, have been applied very successfully with high power conversion efficiencies (PCEs) of 9–12%.^{4–9} Recently, it has been demonstrated that DSSCs can also be constructed from metal-free organic dyes.¹⁰ Because of the high cost of rare Ru metal and the relatively low molar extinction coefficients and tedious purification of Ru-photosensitizers,⁵ metal-free organic sensitizers have become increasingly attractive and widely developed.^{11,12} Nevertheless, the ability to reach higher efficiencies when using metal-free organic dyes remains a challenge, although great progress has been made in this field.^{13–16} The key characteristics for a dye to be used in a DSSC are high absorption over a wide range of the solar spectrum with high molar extinction coefficients, efficient charge separation, redox stability, and suitable

functional groups to interact with the electron sink (TiO₂). Metal-free organic dyes featuring a donor/acceptor structural design were synthesized have particularly wide absorption ranges for DSSC applications.^{11–19} Liquid-crystalline (or mesomorphic) properties can be introduced to organic dyes when 3,4,5-tris(dodecyloxy)phenyl segments are incorporated, resulting in potential applications in flexible electronic materials.^{20–25} Kato et al.²¹ reported conjugated oligothiophene-based polycatenar liquid crystal materials exhibiting electrochromism upon applying an oxidative potential, with layered smectic and columnar structures capable of enhancing hole mobilities up to 0.01 cm² V⁻¹ s⁻¹. Park et al.²² also reported that the mesomorphic organization of a dicyanodistyrylbenzene-based molecule could improve its fluorescence-emitting and semiconducting properties. Therefore, great efforts have been taken toward the preparation and characterization of photo- and electro-active structures based on mesogenic units. The use of various aromatic segments (e.g., fluorene,^{26,27} thiophene^{28,29}) as spacers in organic dyes can improve the photocurrent generation and intramolecular charge separation. Dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT)-conjugated dyes have also exhibited excellent DSSC efficiencies.³⁰ In addition, the DTT unit—a sulfur-rich (three S atoms) and electron-rich building block—increases the planarity of the dye, resulting in longer π -conjugation.^{31,32} Because of restricted intramolecular rotation in fused-ring structures, such as DTT, π -orbital overlap in such conjugated molecules could be maximized to

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enhance intermolecular charge transport.^{33,34} In this study, we prepared dyes featuring a 3,4,5-tris(dodecyloxy)phenyl unit²¹ and a cyanoacrylic acid as electron donor and acceptor units, respectively, with various spacers inserted as the conjugated bridge (Fig. 1). For example, we introduced a fused-DTT unit as a conjugated spacer through which electrons could be transferred efficiently from the donor to the acceptor. In addition to the DTT unit (as a main structure of the conjugated spacer), we also employed bithiophene and bithiazole units to extend the conjugated lengths and, thereby, affect the electron mobilities and absorption spectra. Furthermore, bithiophene unit enhanced the liquid crystallinity of the dye. To increase solubility, we inserted alkyl chains onto bithiazole heterocyclic rings. We were aware, however, that the presence of thiophene rings in the electron-rich segment might not result in sufficient separation between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO); in addition, too many alkyl chains would affect the packing between the layers the molecule, induce molecular aggregation, increase steric hindrance, and decrease charge transfer. If the structure had too many rigid rings, however, its solubility would be impacted, making it harder to dissolve in common solvents with low boiling points and, thereby, complicating device fabrication. Therefore, we also compared the effects of bithiophene^{35–37} and bithiazole³⁸ units. The design of the conjugated system can not only affect the absorption range but also further influence the electron transfer from the excited state to the TiO₂.³⁹ In this study, we suspected that better molecular arrangements and stacking would result if the donor/acceptor molecules exhibited enhanced liquid crystallinity. Therefore, we prepared series of metal-free organic dyes containing DTT³⁷ units with good coplanarity and investigated their mesomorphic and photovoltaic properties.

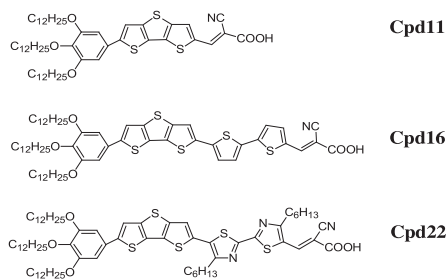


Fig. 1. Chemical structures of the dyes **Cpd11**, **Cpd16**, and **Cpd22**.

2. Results and discussion

2.1. Optical properties

Fig 2 displays the UV–vis absorption and normalized photoluminescence (PL) spectra of **Cpd11**, **Cpd16**, and **Cpd22** as solutions in THF (10^{−5} M); Table 1 lists their corresponding data. The absorption spectra reveal that the signals for **Cpd16** and **Cpd22** were red-shifted relative to those of **Cpd11** after the insertion of the bithiophene and bithiazole units, respectively, to lengthen the conjugated linking structures. The maximum absorption peaks for **Cpd11**, **Cpd16**, and **Cpd22** at 443, 476, and 473 nm, respectively, resulted from intramolecular charge transfer (ICT); that is, for the transition from the 3,4,5-tris(dodecyloxy)benzene donor to the cyanoacrylic acid acceptor. The spectra of the dyes **Cpd16** and **Cpd22** both featured weak $\pi-\pi^*$ transition bands, at 386 and 374 nm, respectively, whereas that of **Cpd11** featured only a single intense band at 443 nm (see Table 1). As expected, the elongated π -conjugations in **Cpd16** and **Cpd22** resulted in narrower $\pi-\pi^*$ energy gaps and spectral red shifts for the $\pi-\pi^*$ transitions. Because the inserted bithiophene and bithiazole units extended the

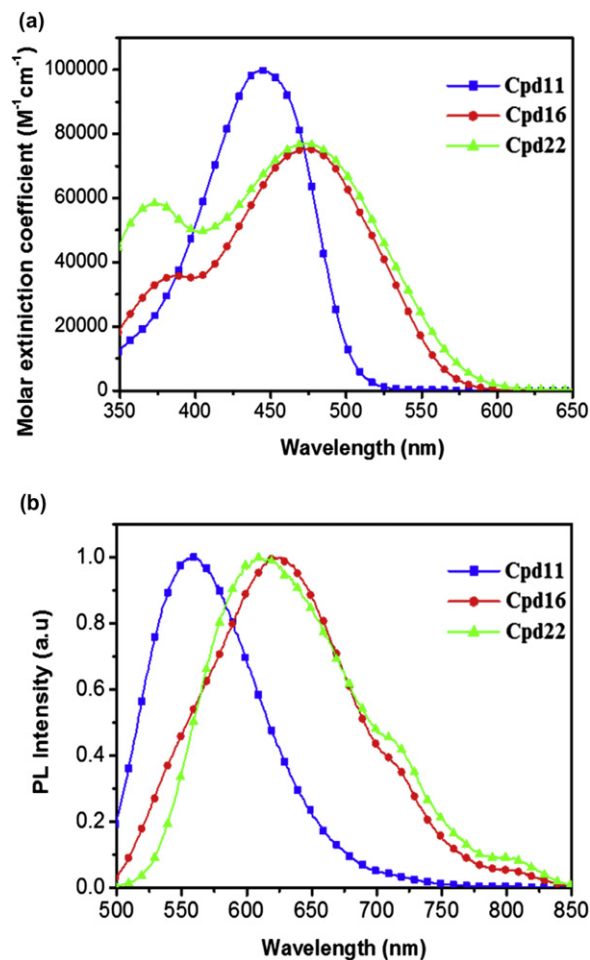


Fig. 2. (a) UV–vis absorption spectra and (b) normalized photoluminescence (PL) spectra of metal-free organic dyes in THF solutions (10^{−5} M).

Table 1
Absorption, emission, and electrochemical properties of the tested dyes

Dye	λ_{abs} (nm) ^a [ϵ (M ^{−1} cm ^{−1})]	λ_{PL} ^a (nm)	Stokes Shift ^b (nm)	E_g^c (eV)	E_{ox}^d (V)	HOMO ^e (eV)	LUMO ^f (eV)
Cpd11	443 (99,000)	557	114	2.45	1.15	−5.70	−3.25
Cpd16	386 (35,700) 476 (75,000)	624	149	2.19	0.71	−5.26	−3.07
Cpd22	374 (58,000) 473 (77,000)	610	135	2.15	0.77	−5.32	−3.17

^a Absorption and PL emission wavelengths recorded in dilute THF solution (10^{−5} M) at room temperature.

^b Stokes shift calculated from the difference between λ_{abs} and λ_{PL} .

^c Optical band gap obtained from the equation $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$.

^d E_{ox} is the oxidation potential.

^e $E_{\text{HOMO}} = [-(E_{\text{ox}} - 0.25) - 4.8]$ eV, where 0.25 V is the value for ferrocene versus Ag/Ag+ and 4.8 eV is the energy level of ferrocene below the vacuum.

^f $E_{\text{LUMO}} = E_{\text{HOMO}} - E_g$.

conjugation lengths in **Cpd16** and **Cpd22**, both dyes exhibited red-shifted and broader absorptions than those of **Cpd11**.⁴⁰ Since **Cpd11** had the narrowest absorption wavelength (Fig. 2a), it also displayed the worst photovoltaic performance among the tested dyes. The molar extinction coefficients of **Cpd16** (476 nm; $\epsilon = 7.50 \times 10^4$ M^{−1} cm^{−1}) and **Cpd22** (473 nm; $\epsilon = 7.70 \times 10^4$ M^{−1} cm^{−1}) at their maximum absorptions are lower than that of **Cpd11** (443 nm; $\epsilon = 9.90 \times 10^4$ M^{−1} cm^{−1}), because the inserted bithiophene and bithiazole units decreased the coplanarity of the acceptor and

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