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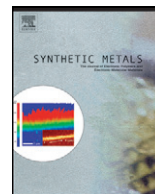


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Synthesis, photophysical and electroluminescent properties of donor–acceptor–donor molecules based on α -cinnamoyl cyclic ketene dithioacetals

Ping Peng, Yinhua Zhou, Kunpeng Li, Houyu Zhang, Haijian Xia, Yixin Zhao, Wenjing Tian*

Key Lab for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130023, PR China

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ABSTRACT

New symmetrical π -conjugated donor–acceptor–donor functionalized molecules consisting of different electron-donating moieties but same α -cinnamoyl cyclic ketene dithioacetals (CCKDA) acceptor have been synthesized. The photophysical properties of these compounds indicate that the absorption and emission result from the intramolecular charge-transfer between the donor and the acceptor. Cyclic voltammetry data show that the band gaps of the compounds vary by introducing different donor moieties. Density functional theory calculations provide an insight into the electronic structure of the molecules. The double-layer electroluminescent devices are fabricated by using these molecular materials as light emitting layer. The electroluminescent performance of the device suggests that these donor–acceptor–donor molecules can be good candidates for the application in organic light-emitting diodes.

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1. Introduction

In recent years, the development of conjugated organic materials has made great progress because of their applications as photoactive and electroactive materials. Donor–acceptor (D–A) organic molecule is one of the most important conjugated organic materials, which have attracted considerable attention as electroluminescent (EL) materials for organic light-emitting diodes (OLEDs) [1–5]. In these compounds the electron-donating and electron-accepting groups are connected through a π -conjugated linker, whereby the donor moiety facilitates hole injection and transport, the acceptor moiety facilitates electron injection and transport [6–8]. The merit of the donor–acceptor materials is that their physical and chemical properties can be modified by tuning different donor moieties or/and acceptor moieties. But the D–A molecules with symmetrical structures have been researched sparsely.

The present paper reports the synthesis and properties of a novel family of CCKDA derivatives with symmetrical Donor–Acceptor–Donor (D–A–D) structures. As we report now, a simple and low-cost way by Claisen–Schmidt condensation reactions between the donor-containing aldehydes and the electron-withdrawing CCKDA is applied. Carbazole, *N,N*-

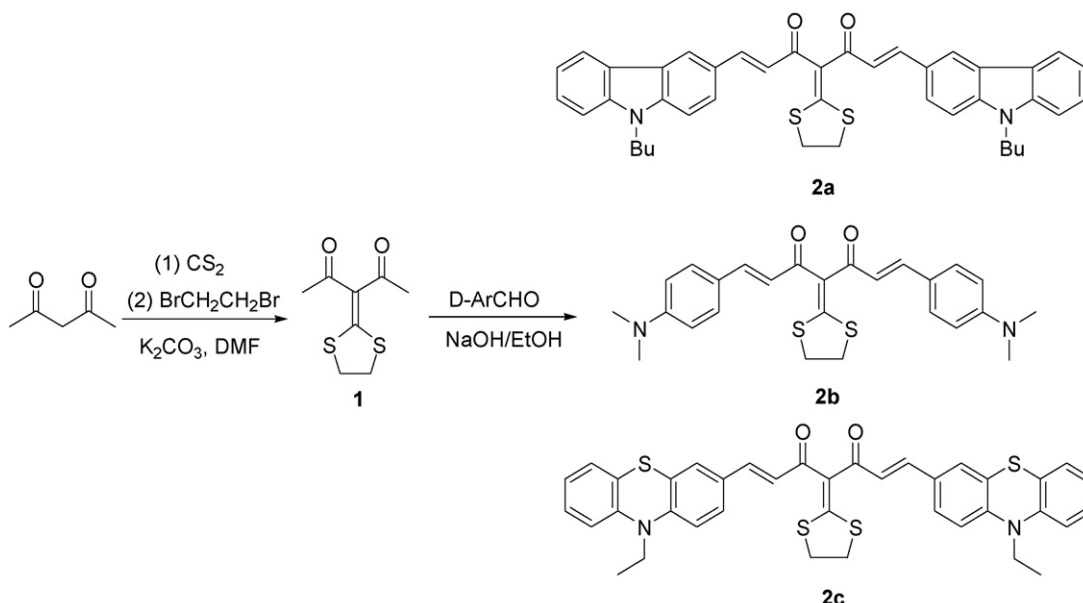
dimethylbenzenamine and phenothiazine are adopted as donors as a result of their well thermal and electrochemical stability and donating abilities [9]. α -Oxo Ketene Dithioacetal (OKD) is used as acceptor. The UV–vis absorption and photoluminescence (PL) of these compounds suggest significant ICT behaviour and solvatochromism. The electrochemical analysis manifests that the energy level of these compounds can be changed by altering different donor moieties. Their photovoltaic properties were studied previously [10]. Here, the EL properties of the D–A–D molecules prove the intense possibility of using these materials in OLED.

2. Experimental Section

All chemicals, reagents, and solvents were used as received from commercial sources without further purification. ^1H NMR spectrum was recorded on an AVANCE 500 spectrometer with tetramethylsilane (TMS) as the standard. UV–vis absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. The PL spectra were recorded on Shimadzu RF-5301PC fluorescence spectrophotometer. Differential scanning calorimetry (DSC) analysis was carried out with a NETZSCH (DSC-204) instrument at $10^\circ\text{C min}^{-1}$, while flushing with nitrogen. The EL measurements of these derivatives were performed with a CHI620B electrochemical workstation (CH. Instruments Inc., USA). The EL spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer. The CCKDA derivatives were prepared according to Scheme 1.

* Corresponding author. Tel.: +86 431 85166212; fax: +86 431 85193421.

E-mail address: wjtian@mail.jlu.edu.cn (W. Tian).



Scheme 1. Synthesis of CCKDA derivatives (**2a–2c**).

3-(1,3-Dithiolan-2-ylidene)pentane-2,4-dione (**1**)

Pentane-2,4-dione (5.13 ml, 50 mmol) and anhydrous K_2CO_3 (13.8 g, 100 mmol) were stirred in DMF (30 ml) for 30 min at room temperature. Then CS_2 (3.31 ml, 55 mmol) was added. The color of solution turned into red. After 1 h, 1,2-dibromoethane (4.74 ml, 55 mmol) was added dropwise within 10 min. The mixture was allowed to warm to room temperature and stirred for 8 h and then poured into ice-water (500 ml) under stirring. The white precipitated solid was collected by filtration, washed with water and dried in vacuo to afford the product (9.49 g, 94%).

General synthetic procedure for CCKDA derivatives

These compounds were synthesized via the Claisen–Schmidt condensation of compound **1** with aromatic aldehydes. Compound **1** (1.0 equiv.), aromatic aldehydes (2.0 equiv.), NaOH (2.0 equiv.) were stirred in ethanol (3 ml) for 12 h. After the starting material compound **1** was consumed as indicated by TLC, the resulting mixture was collected by filtration, washed with diethyl ether and dried in vacuo. The final product was obtained after column chromatographic purification method on silica gel.

2a

(1E,6E)-1-(9-Butyl-9H-carbazol-2-yl)-7-(9-butyl-9H-carbazol-3-yl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione

Yellow solid. Yield: 72.5%. 1H NMR ($CDCl_3$, 500 MHz, TMS): δ 0.88 (6H, t, CH_3), 1.32 (4H, m, CH_2), 1.76 (4H, m, CH_2), 3.41 (4H, s, SH_2), 4.21 (4H, t, CH_2), 7.09 (2H, t, Ar-H), 7.15 (2H, d, CH), 7.26 (2H, d, Ar-H), 7.34 (2H, d, Ar-H), 7.41 (2H, t, Ar-H), 7.67 (2H, d, Ar-H), 7.88 (2H, d, Ar-H), 7.99 (2H, d, CH), 8.24 (2H, s, Ar-H). Elemental analysis calcd. (%) for $C_{42}H_{40}N_2O_2S_2$: C 75.41 H 6.03, N 4.19; found: C 75.32, H 6.08, N 4.12.

2b (1E,6E)-1,7-Bis(4-(dimethylamino)phenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione

Red solid. Yield: 81.1%. 1H NMR ($CDCl_3$, 500 MHz, TMS): δ 2.99 (12H, s, CH_3), 3.35 (4H, s, SH_2), 6.61 (4H, d, Ar-H), 6.82 (2H, d, CH), 7.41 (4H, d, Ar-H), 7.67 (2H, d, CH). Elemental analysis calcd. (%) for $C_{26}H_{28}N_2O_2S_2$: C 67.21, H 6.07, N 6.03; found: C 67.15, H 6.10, N 5.99.

2c (1E,6E)-4-(1,3-Dithiolan-2-ylidene)-1,7-bis(10-ethyl-10H-phenothiazin-3-yl)hepta-1,6-diene-3,5-dione

Scarlet solid. Yield: 65.6%. 1H NMR ($CDCl_3$, 500 MHz, TMS): δ 1.38 (6H, t, CH_3), 3.37 (4H, s, SH_2), 3.89 (4H, m, CH_2), 6.77 (2H, d, Ar-H), 6.83 (2H, d, CH), 6.84 (2H, d, Ar-H), 6.89 (2H, t, Ar-H), 7.05 (2H, d, Ar-H), 7.12 (2H, m, Ar-H), 7.21 (2H, s, Ar-H), 7.27 (2H, d, Ar-H), 7.57 (2H, d, CH). Elemental analysis calcd. (%) for $C_{38}H_{32}N_2O_2S_4$: C 67.42, H 4.76, N 4.14; found: C 67.37, H 4.81, N 4.08.

3. Results and discussion

3.1. Photophysical properties

Fig. 1 shows the UV–vis absorption and PL spectra of the three compounds in CH_2Cl_2 at room temperature. In their absorption spectra, the high-energy transition bands around 300 nm are attributed to $n-\pi^*$ transition and discrete bands at 390–425 nm are deduced to ICT from the donor to the acceptor. The absorption maxima of the three compounds are at 396 nm, 417 nm and 427 nm, respectively, which gradually increase with the enhancement of electron-donating abilities of donors. Among the three donors, the

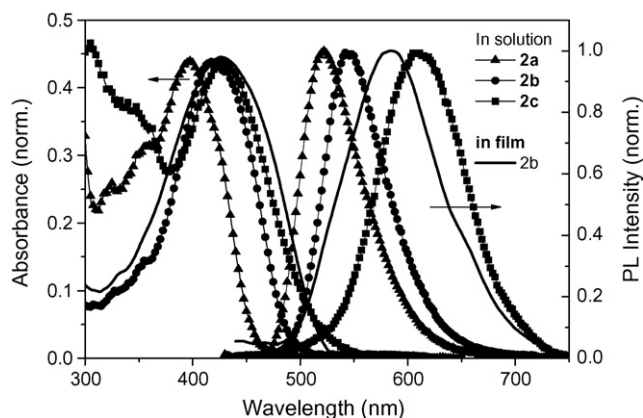


Fig. 1. Normalized UV–vis absorption and photoluminescence spectra of derivatives (**2a–2c**) in CH_2Cl_2 .

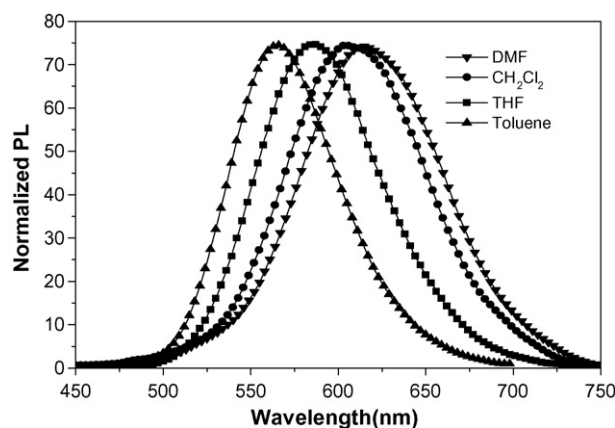


Fig. 2. PL emission spectra of **2c** in solvents with different polarity.

carbazole has the least electron-donating ability, the phenothiazine has the most electron-donating ability and the electron-donating ability of *N,N*-dimethylbenzamine is between them. Therefore the absorption maximum of **2a** with carbazole as donor locates in the shortest wavelength 396 nm, and that of **2b** locates in 417 nm while that of **2c** locates in 427 nm. A similar trend is observed in their fluorescence spectra with the emitting wavelength increasing in the order of **2a** (522 nm) < **2b** (543 nm) < **2c** (605 nm) because of the electron-donating ability improvement of the aromatic donor [11]. The emission colors of the compounds are changing from green to red when carbazole is replaced by phenothiazine. It means that the emission color of the D–A–D molecules could be adjusted by introducing different donor groups, which is an easy way to realize different color emission of OLED [12]. Fig. 1 also shows the absorption and PL spectra of **2b** in film. It can be seen that the red shift can both be seen in absorption and PL spectra from in solution to film, which is due to the stacking aggregation in the film. In addition, all the emission spectra of these compounds display positive solvatochromism in different solvents. Fig. 2 shows the PL of **2c** in solvent with different polarity (toluene, THF, CH₂Cl₂, DMF). The emission peaks of **2c** are shifted significantly from 564 nm to 614 nm with increasing the solvent polarity from toluene to DMF. The distinct solvatochromism is by reason of the significant interaction between the ICT excited state and the solvent molecules [13]. The photophysical data of the three compounds are summarized in Table 1.

3.2. Thermal properties

The thermal properties of the three compounds were investigated by DSC. Fig. 3 shows their DSC curves during the second heating–cooling cycle. Their glass transition temperature (*T_g*) can be obtained to be 126°C, 99°C and 129°C for **2a**, **2b** and **2c**, separately, which shows the D–A molecules have relatively good thermal stability.

Table 1
Optical properties of the compounds

Compounds	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)			
		Toluene	THF	CH ₂ Cl ₂	DMF
2a	396	479	512	522	550
2b	417	516	531	543	569
2c	427	564	586	605	614

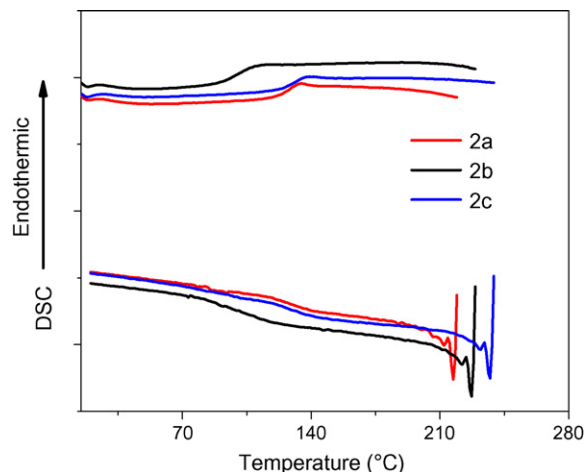


Fig. 3. DSC curves of the three samples during the second heating–cooling cycle.

Table 2
Electrochemical data and energy level parameters for the compounds in DMF

Compounds	E_{ox}^{a}	$E_{\text{red}}^{\text{a}}$	HOMO (eV)	LUMO (eV)	E_{g}
2a	0.89	−1.83	−5.39	−2.67	2.72
2b	0.66	−1.88	−5.16	−2.62	2.54
2c	0.68	−1.72	−5.18	−2.78	2.40

3.3. Electrochemical properties

The redox behaviors of these compounds are investigated by cyclic voltammetry (CV) in dry DMF. Fig. 4 shows the CV curve of the three compounds. There is a notable reduction peak in CV curve which originates from the reduction of the acceptor group [14]. The lowest unoccupied molecular orbital (LUMO) levels of the three compounds can be calculated according to the formula: $E_{\text{LUMO}} = e \times E_{\text{red}} + 4.5 \text{ eV}$, where E_{red} is the reduction potential in volt versus the normal hydrogen electrode potential [15]. The highest occupied molecular orbital (HOMO) level can be estimated by subtracting its optical band gap E_{g} from the LUMO level, while E_{g} is deduced from the absorption edge [15,16]. Thus, the LUMO and HOMO level of **2a** are calculated to be −2.67 eV and −5.39, respectively. Detailed data for CV and the energy level parameters are listed in Table 2. As described in Table 2, the reduction potential of those compounds with the same acceptor is approximately the same, so their LUMO levels are similar. The UV–vis absorption spectra indicate that the stronger of the electron-donating ability of the

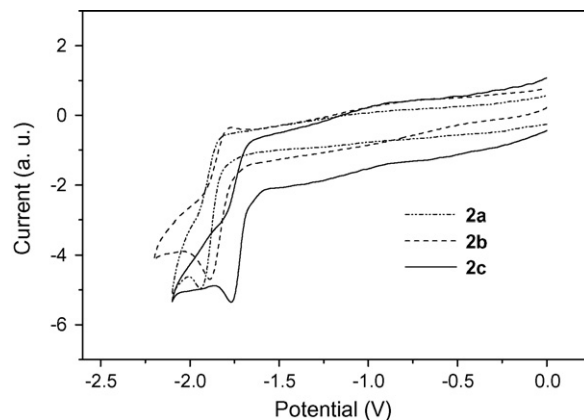


Fig. 4. The CV of compounds **2a**, **2b** and **2c** in DMF.

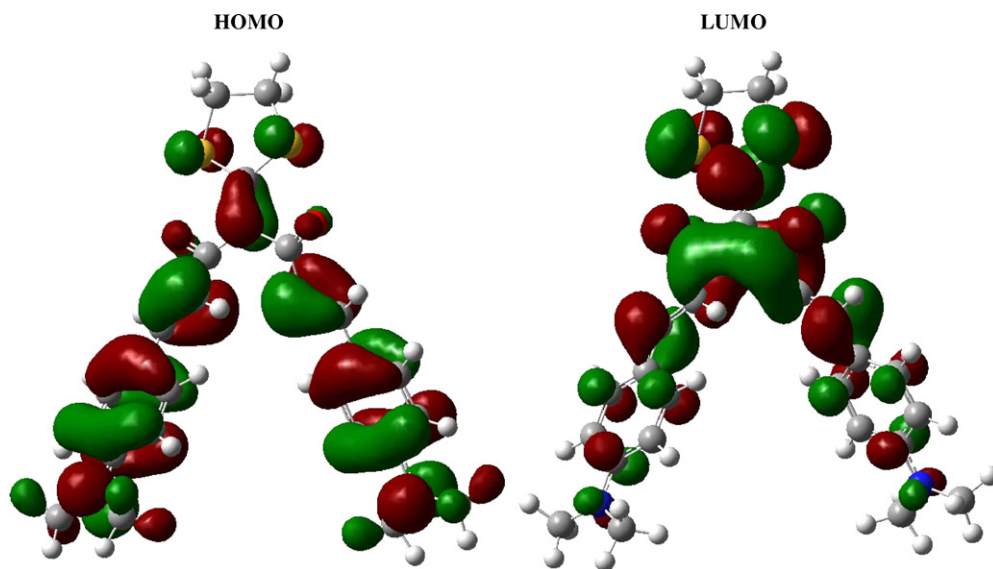


Fig. 5. HOMO and LUMO orbitals in the optimized ground-state structure of **2b**.

donor, the narrower of the optical band gap of the molecule. Consequently, the change of the electron-donating ability of the donor will lead to the difference of the HOMO level.

3.4. Quantum-chemical calculation

In order to well understand the optical properties of these compounds, quantum-chemical calculations are performed. We take **2b** as an example. The geometries of **2b** are optimized using the Gaussian 03 program [12] at the B3LYP/6-31G* level. Fig. 5 shows the calculated the optimized ground-state structure of **2b** and the electron distribution in the frontier MOs reveals that the HOMO is localized on the *N,N*-dimethylbenzenamine donor moiety, while LUMO is localized on the α -Oxo Ketene Dithioacetal acceptor moiety. So the ICT in the excited states of **2b** can be expected, which explains the sensitivity of its emission wavelength towards the polarity of the solvent. Furthermore, the solvent of increasingly polar stabilizes the excited state and leads to the emitting peak to red-shift [17,18].

3.5. Electroluminescence properties

We select **2b** as an example to investigate the electroluminescent performance via fabricating a double-layer OLED (ITO/PVK: **2b** (6%, w/w)/Alq₃/LiF/Al). Here, poly(9-vinylcarbazole) (PVK) is adopted as the host for CCKDA molecules because of its well-known hole-transporting property, film-forming ability and capability of dissolving small molecules in high concentrations [19,20]. The HOMO and LUMO energy levels of PVK are located at -5.9 eV and -2.4 eV separately [18]. Regarding our D-A-D material **2b**, its HOMO and LUMO energy levels locate at about -5.2 eV and -2.7 eV separately. This means the efficient energy transfer could occur between the PVK and our D-A-D molecules. And Alq₃ acts as an electron-transport layer and a hole block layer. We fabricated devices with different doping concentration of compound **2b** in PVK host. Table 3 shows the EL performance of the devices with doping concentration of compound **2b**. It can be seen that the best performance was achieved in the device with the concentration of **2b** of 6%. This device exhibits turn voltage of 10 V, the maximum

Table 3

The EL properties of device ITO/PVK:**2b** (w/w)/Alq₃/LiF/Al with different **2b** concentration in PVK host

(2b wt.%) in PVK: 2b	EL _{max} (nm)	V _{on} (V)	L _{max} (cd/m ²) (V)	Max. current efficiency (cd/A)
2%	515	7.5	462.7 (21)	1.21
4%	522	7	624.3 (21)	1.27
6%	520	6.5	614.6 (20.5)	1.50
8%	528	6	498.7 (21)	1.18
10%	528	7	431.6 (20.5)	0.49

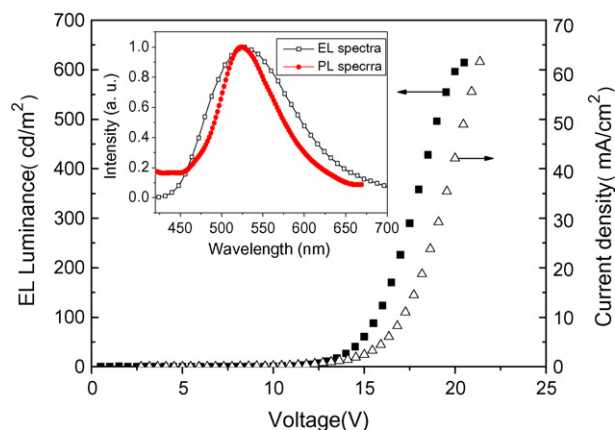


Fig. 6. Luminescence-voltage-current density characteristics of the device with **2b** to be used as emission layer. Inset is the EL emission.

luminance of 614.6 cd/m^2 at 20.1 V , and the efficiency of 1.5 cd/A (Fig. 6). We combined the PL and EL spectra of compound **2b** (6%): PVK in the inset of Fig. 6. It can be seen that they are quite similar. So, we can conclude that the EL emission originates from ICT state as PL emission.

4. Conclusion

This study reports the synthesis and characterization of a novel family of CCKDA molecules with symmetrical structure D-A-D.

The photophysical properties are of a significant ICT behavior and solvatochromism. The electrochemical properties indicate that the energy level parameters can be changed by introduction of different donors. Quantum-chemical calculation of electronic structure shows that the levels of HOMO and LUMO of CCKDA molecules are highly localized on the donor and acceptor moieties, respectively. In addition, compound **2b** is used to fabricate a double-layer OLED device that exhibits good performance. And we may get different EL color by changing different donors. All the results reveal that the D–A molecules may find promising applications in OLED.

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