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Design and synthesis of 1,4-bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(alkoxy)benzenes as red organic electroluminescent PPV analogs

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Abstract

A series of 1,4-distyrylbenzene derivatives containing 1,1-dicyanovinyl moieties were designed as poly-*p*-phenylenevinylene analogs to obtain the red electroluminescence assisted by the computational results. Based on the subsequent synthesis and optical studies, the present work indicated that introduction of 1,1-dicyano group as electron receptor in PPV skeleton could shift the electroluminescence significantly to the red region. The present work has shown a successful strategy to tune the emission of PPV analogs based on the theoretical design and organic synthesis.

Keywords: Red luminescence; 1,4-Distyrylbenzene derivatives; 1,1-Dicyanovinyl

1. Introduction

The conjugated poly-*p*-phenylenevinylene (PPV) polymers have been widely investigated due to the interests in many areas of materials research, such as in organic light-emitting displays (LEDs) [1], field-effect transistors (FETs) [2], and photovoltaics (solar cells) [3]. Generally, the single PPV oligomers were most appreciated because they could avoid a random distribution in terms of molecular weight and improve the purities [4]. It means that the single oligomers could provide a more easy way to develop precise structure–property relationships, which are appreciated for both practical applications [5] and theoretical approaches [6]. However, it still remained as a challenge to realize full-color displays required the three elemental colors of red, green, and blue emitters through molecular design and modifications of the PPV analogs. Compared to the striking successes in OLED of the other two colors, the situation for red OLEDs is far behind in terms of both color purity and efficiency [7].

In designing the PPV polymers, side-chain substituents attached on the main-PPV chain are very important moiety closely related to their EL performance. Generally, levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) could be tuned by the electron-donating or -withdrawing substituents, which determine energy barriers of charge injection and a band gap correlated with an emission color [8]. Therefore, introduction of an appropriate electron-withdrawing group as electron acceptors in the PPV skeleton should be an alternative to modulate the luminescence of OLED to the different wavelengths. Such approach has been shown in the CN–PPV oligomers with blue-green or yellow EL, where the cyano groups were attached to the vinylic double bond [8,9]. As a stronger electron-withdrawing substituent, the dicyanovinyl group has been introduced in a series of isophorone-based EL devices with red luminescence [7a]. However, the influence of dicyanovinyl group on the PPV-based EL still remains unknown in our best knowledge.

In present contribution, we designed and synthesized a series of 1,4-bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(alkoxy)-benzenes **1** (Scheme 1). Assisted by the computational studies, we first investigated the absorption of **1** in the ground state and

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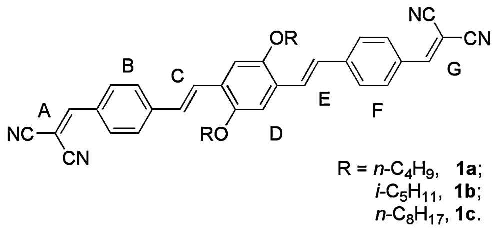


Scheme 1. Molecular structures of the present PPV analogs.

fluorescence in the singlet excited states using TD-DFT methods. The emission of **1** was theoretically evaluated in 595.3 nm (Table 1), which initialized our studies to the development of the new series of red electroluminescent organic molecules. On the other hand, the electron densities of HOMO and LUMO of **1** in the ground and first singlet excited states have little change in the alkoxy substituents, which provided us an easy way to improve the solubility of **1** in organic solvents through modification of the alkoxy substituents without significant effects on the optical properties of **1**. The present work exemplified the successful strategy to modulate the luminescence of the single oligomer to the red regions through a rational derivation of the PPV skeletons on the basis of both theoretical predication and organic synthesis.

2. Experimental part

2.1. Materials and instruments

All chemicals were purchased from Aldrich and used as received without further purification. For chromatography, 100–200 mesh silica gel (Qingdao, China) was employed. UV–vis absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3010) and fluorescence spectra were determined on a fluorescence spectrophotometer (RF-540). NMR spectra were recorded at a Bruker AV-300 spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane (TMS) as the internal standard. IR spectra were recorded with a Varian FT-IR 1730 spectrophotometer. Mass spectra were obtained on a MALDI TOF mass spectrometer.

*2.2. Synthesis of 2-(p-methylbenzylidene)malononitrile (**2**)*

A mixture of malononitrile (6.69 g, 100 mmol) and *p*-methylbenzaldehyde was heated to 150 °C and remained for 3 h at the temperature. After cooling, the resulting solution was filtered and then dried in the vacuum. Recrystallization from CH_2Cl_2 and ethanol provided a purple solid as product (14.6 g, yield: 86%). M.p. 119–122 °C. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.83$ (d, $J = 8.1$ Hz, 2H), 7.73 (s, 1H), 7.35 (d, $J = 7.9$ Hz, 2H), 2.47 (s, 3H).

*2.3. 2-(p-Bromomethyl benzylidene)malononitrile (**3**)*

To a solution of **1** (2.35 g, 13.97 mmol) and *N*-bromosuccinimide (2.98 g, 16.74 mmol) in CCl_4 (25 mL) was added catalytic amount of benzoyl peroxide. The reaction mixture was refluxed with stirring for 3 h. After cooling and filtration, the solvents were evaporated under vacuum. The product was obtained as a yellow solid (3.07 g, yield: 89%).

*2.4. 1-(1,1-Dicyanovinyl)-4-(triphenylphosphoniomethyl)benzene bromide (**4**)*

A solution of **2** (3.85 g, 15.58 mmol) and PPh_3 in CH_2Cl_2 (50 mL) was refluxed for 6 h. After cooling and filtration, a white solid was obtained as product (4.02 g, yield: 50.6%). ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 8.48$ (s, 1H), 7.91 (m, 3H), 7.8–7.7 (m, 14H), 7.18 (d, $J = 7.9$ Hz, 2H), 2.49 (s, 2H).

*2.5. 1,4-Dialkoxybenzene (**5**)*

To a solution of *p*-hydroquinone and KOH (2.0 eq.) in DMSO, 1-bromobutane (2.0 eq.) was added and stirred at 75 °C for 4 h. The reaction mixture was poured into water. After extracted with CH_2Cl_2, the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvents were removed under reduced pressure. The residue was purified with chromatography with chloroform as eluent. The product was obtained as a white sheet solid.

*2.5.1. 1,4-Di-(n-butoxy)benzene (**5a**)*
Yield: 73%. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 6.84$ (s, 4H), 3.93 (t, $J = 6.5$ Hz, 4H), 1.78–1.75 (m, 4H), 1.53–1.52 (m, 4H), 0.99 (t, $J = 7.3$ Hz, 6H).

*2.5.2. 1,4-Di-(i-pentoxy)benzene (**5b**)*
Yield: 70%. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 6.83$ (s, 4H), 3.94 (t, $J = 6.7$ Hz, 4H), 1.84–1.80 (m, 2H), 1.67–1.64 (m, 4H), 0.96 (d, $J = 5.8$ Hz, 12H).

Table 1
Frontier molecular orbital (FMO) components of **1c** (%) in the ground and first singlet excited states

MO	Compositions of FMOs in the ground state							λ_{abs} (nm)	Compositions of FMOs in the first singlet excited state							λ_{em} (nm)
	A	B	C	D	E	F	G		A	B	C	D	E	F	G	
LUMO + 2	16.7	6.8	12.1	28.8	12.1	6.8	16.7	342.8	21.1	6.3	8.2	28.9	8.2	6.3	21.1	595.3
LUMO + 1	29.0	14.8	3.9	4.5	3.9	14.8	29.0	386.2	24.9	18.8	4.5	3.5	4.5	18.8	24.9	428.4
LUMO	20.9	14.6	8.3	12.3	8.3	14.6	20.9	506.8	12.5	16.0	10.8	21.2	10.8	16.0	12.5	
HOMO	4.6	8.7	11.4	50.5	11.4	8.7	4.6		3.2	11.1	14.5	42.3	14.5	11.1	3.2	
HOMO − 1	3.5	5.0	3.5	75.9	3.5	5.0	3.5		11.6	24.3	11.2	5.9	11.2	24.3	11.6	
HOMO − 2	14.9	19.6	11.0	9.0	11.0	19.6	14.9		4.0	5.9	1.2	77.7	1.2	5.9	4.0	

2.5.3. 1,4-Di-(n-octoxy)benzene (**5c**)

Yield: 69%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.84$ (s, 4H), 3.92 (t, $J = 6.6$ Hz, 4H), 1.79–1.74 (m, 4H), 1.46–1.43 (m, 4H), 1.33–1.29 (m, 16H), 0.91 (t, $J = 6.6$ Hz, 6H).

2.6. 2,5-Bis(bromomethyl)-1,4-dialkoxybenzene (**6**)

To a stirred solution of **4** (11.63 mmol) and paraformaldehyde (4.0 eq.) in glacial acetic acid, a mixture of 40% HBr (26.5 eq.) and glacial acetic acid was added. The mixture remained stirring for 24 h at 80 °C under nitrogen atmosphere. After cooling down, the reaction mixture was poured into water and then neutralized with sodium hydroxide. After extraction by chloroform and evaporation of organic layer under reduced pressure, recrystallization from petroleum ether and CH_2Cl_2 afforded a pale-yellow needles as product.

2.6.1. 2,5-Bis(bromomethyl)-1,4-di-(n-butoxy)benzene (**6a**)

Yield: 71%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.87$ (s, 2H), 4.55 (s, 4H), 4.01 (t, $J = 6.3$ Hz, 4H), 1.83–1.80 (m, 4H), 1.57–1.52 (m, 4H), 1.00 (t, $J = 7.3$ Hz, 6H).

2.6.2. 2,5-Bis(bromomethyl)-1,4-di-(i-pentoxy)benzene (**6b**)

Yield: 69%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.86$ (s, 2H), 4.53 (s, 4H), 4.02 (t, $J = 6.5$ Hz, 4H), 1.89–1.85 (m, 2H), 1.74–1.72 (m, 4H), 0.98 (d, $J = 4.6$ Hz, 12H).

2.6.3. 2,5-Bis(bromomethyl)-1,4-di-(n-octoxy)benzene (**6c**)

Yield: 71%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.87$ (s, 2H), 4.54 (s, 4H), 4.00 (t, $J = 6.4$ Hz, 4H), 1.85–1.82 (m, 4H), 1.53–1.50 (m, 4H), 1.37–1.31 (m, 16H), 0.91 (t, $J = 6.6$ Hz, 6H).

2.7. 2,5-Dialkoxyterephthaladehyde (**7**)

To a mixture of **5** and hexamethylenetetramine (3.6 eq.) in ethanol in refluxing, 50% aqueous HOAc was added dropwise for 2 h. After further refluxing for 1 h, the mixture was subjected to pour into water and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$. After filtering, the solvents were removed under reduced pressure. The crude product was purified by a silica gel column with petroleum ether and dichloromethane as eluent to give rise yellow-green crystal as product.

2.7.1. 2,5-Di-(n-butoxy)terephthaladehyde (**7a**)

Yield: 53%. M.p. 93–96 °C ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.53$ (s, 2H), 7.45 (s, 2H), 4.11 (t, $J = 8.9$ Hz, 4H), 1.86–1.82 (m, 4H), 1.57–1.51 (m, 4H), 1.0 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 189.4$, 155.2, 129.3, 111.6, 68.9, 31.1, 19.2, 13.8.

2.7.2. 2,5-Di-(i-pentoxy)terephthaladehyde (**7b**)

Yield: 56%. M.p. 79–82 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.50$ (s, 2H), 7.43 (s, 2H), 4.11 (t, $J = 6.5$ Hz, 4H), 1.83–1.81 (m, 2H), 1.76–1.73 (m, 4H), 0.97 (d, $J = 6.5$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 189.9$, 152.2, 131.3, 110.9, 68.6, 29.5, 21.8, 14.1.

2.7.3. 2,5-Di-(n-octoxy)terephthaladehyde (**7c**)

Yield: 62%. M.p. 69–72 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.50$ (s, 2H), 7.43 (s, 2H), 4.12 (t, $J = 6.4$ Hz, 4H), 1.86–1.82 (m, 4H), 1.51–1.48 (m, 4H), 1.36–1.30 (m, 16H), 0.92 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 189.1$, 155.3, 130.2, 112.4, 68.0, 31.9, 29.7, 26.1, 22.5, 19.2, 13.8.

2.8. 1,4-Bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(alkoxy)benzene (**1**)

To a THF solution of **3** (2.0 eq.) and potassium *t*-butoxide (2.4 eq.), a solution of **6** in THF was added dropwise under nitrogen atmosphere. After addition, the mixture was kept stirring for 30 min at room temperature and further refluxed for 24 h. After cooling and condensed under reduced pressure, the residue was diluted with water and then extracted with chloroform. Organic layer was evaporated under reduced pressure. The residual crude product was then purified by column chromatography using ethyl acetate and petroleum ether as eluent. Evaporation provided products as dark red solid.

2.8.1. 1,4-Bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(n-butoxyl)benzene (**1a**)

Yield: 50%. IR (KBr, cm^{-1}): 2359, 2341, 1569, 1538, 1521, 1322, 1212, 1178. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.92$ (d, $J = 8.1$ Hz, 4H), 7.72 (s, 2H), 7.66 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 10.1$ Hz, 2H), 7.12 (d, $J = 10.1$ Hz, 2H), 4.07 (t, $J = 8.9$ Hz, 4H), 1.86–1.82 (m, 4H), 1.55–1.51 (m, 4H), 1.01 (t, $J = 7.4$ Hz, 6H). MS *m*/*z* (%): 522.2 (M^+, 80).

2.8.2. 1,4-Bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(i-pentoxyl)benzene (**1b**)

Yield: 44%. IR (KBr, cm^{-1}): 2359, 2341, 1575, 1569, 1506, 1521, 1457, 1419, 1180. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.94$ (d, $J = 8.2$ Hz, 4H), 7.73 (s, 2H), 7.69 (d, $J = 16.5$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 4H), 7.22 (d, $J = 16.5$ Hz, 2H), 7.15 (s, 2H), 4.10 (t, $J = 6.4$ Hz, 4H), 1.93–1.91 (m, 2H), 1.34–1.31 (m, 4H), 0.90 (d, $J = 6.6$ Hz, 12H). MS *m*/*z* (%): 578.3 (M^+, 100).

2.8.3. 1,4-Bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(n-octoxyl)benzene (**1c**)

Yield: 59%. IR (KBr, cm^{-1}): 2925, 2221, 1571, 1538, 1182. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.94$ (d, $J = 8.2$ Hz, 4H), 7.73 (s, 2H), 7.69 (d, $J = 16.5$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 4H), 7.22 (d, $J = 16.5$ Hz, 2H), 7.15 (s, 2H), 4.10 (t, $J = 6.4$ Hz, 4H), 1.93–1.91 (m, 4H), 1.43–1.39 (m, 4H), 1.36–1.30 (m, 16H), 0.90 (d, $J = 6.6$ Hz, 6H). MS *m*/*z* (%): 691.3 (M^+, 100).

2.9. Computational methods

The GAUSSIAN 98 [10] series of programs were used for all calculations. All molecules were fully optimized in the ground state using the hybrid density functional B3LYP level [11] of theory with the 6-31G-(d) basis set. The structures in the ground state were fully optimized followed by frequency analysis. Optimization of the geometry in the first singlet excited state (S_1) was performed using configuration interaction with all singly excited determinants [12] (CIS) in the frozen-core approximation and 6-31G(d) basis set. To obtain estimates of the vertical electronic excitation energies including absorption and fluorescence maximum, time-dependent density functional theory (TD-DFT) [13] was used with the same basis set.

2.10. Fabrication of light-emitting devices

Prior to the fabrication, the commercially available ITO glass was ultrasonically cleaned with detergent, rinsed in water, and finished with the UV-ozone method. The organic thin film of **1c** and the Al top electrodes (area × mm^2) were deposited by vacuum evaporation (about 5×10^{14} Torr).

TM-350 surface profiler was used to determine the layer thickness, and the *I*−*V* characteristics were measured by an electrometer (Model 2400 Source Meter). EL spectra of the devices were recorded on PR-560. These measurements were all carried out in an ambient atmosphere.

3. Results and discussions

The structures of the designed PPV analogs **1a**−**c** are shown in Scheme 1, with labels A−G designating the different moieties. To determine the contributions of the different moieties to the molecular orbitals of the ground and first singlet excited state, frontier molecular orbital analysis was evaluated based on the optimized structures (Table 1). Theoretical calculations disclosed that the internal charge transfer (ICT) excited state should be evolved upon excitation, meanwhile the most electronic densities of the lowest unoccupied molecular orbital (LUMO) were populated at the dicyanovinyl moieties of **1**. The dicyanovinyl groups (A and G) were thus proposed as the electron acceptors. The absorption maximum and fluorescence emission of **1** were estimated as 506.8 and 595.3 nm, respectively. On the other hand, the alkoxy groups of **1** have little contributions to the electronic properties of both the ground state and the first singlet excited state, which provided a solid basis to modulate the solubilities of **1** in organic solvents through the alternation of the alkoxy substituents (Fig. 1).

Preparation of the three PPV analogs, 1,4-bis[4-(1,1-dicyanovinyl)styryl]-2,5-bis(*n*-butoxy, *i*-pentoxy and *n*-octoxy)-benzenes (**1a**−**c**), was achieved utilizing Wittig reaction of dialdehyde bearing different alkoxy substituents with a ylide bearing dicyanovinyl group as the key step (Scheme 2). The solubilities of **1** in $CHCl_3$ increased with the alkoxy chains, which could be ascribed to the introduction of more bulky alkoxy group in PPV structures.

Both UV−vis absorption and fluorescence spectra of **1c** in $CHCl_3$ are shown in Fig. 2. Accordingly, the calculated maximum of absorption and emission were in good agreement to the experimental data. It could be found that there is good overlap between the EL spectrum of Alq_3 and the absorption spectra of the red emitter, which suggested that efficient Förster energy transfer from the Alq_3 host to the red dopants could be expected in EL devices. Although the experimental fluorescence in 584 nm corresponded to the orange region, the subsequently fabricated LED device using **1c** as dopant

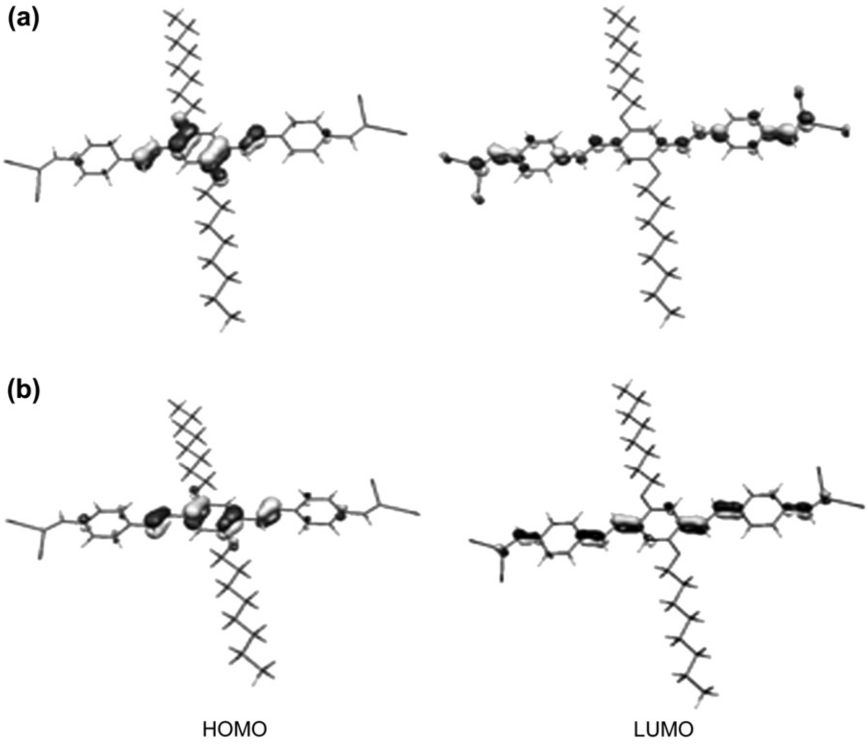
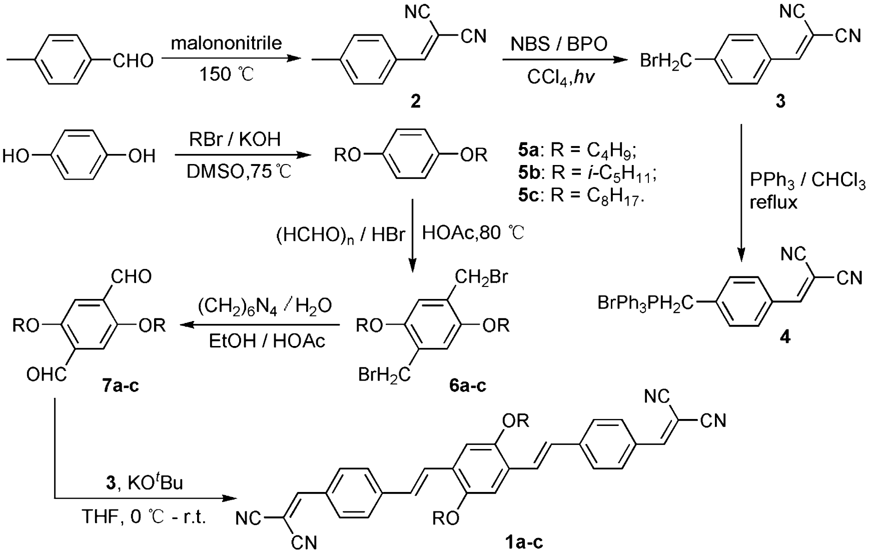


Fig. 1. HOMO and LUMO of **1c** at the B3LYP/6-31(d) level of theory calculated by Gaussian 98. (a) The ground state; (b) the first singlet excited state.



Scheme 2. Synthesis of the present PPV analogs with dicyanovinyl group.

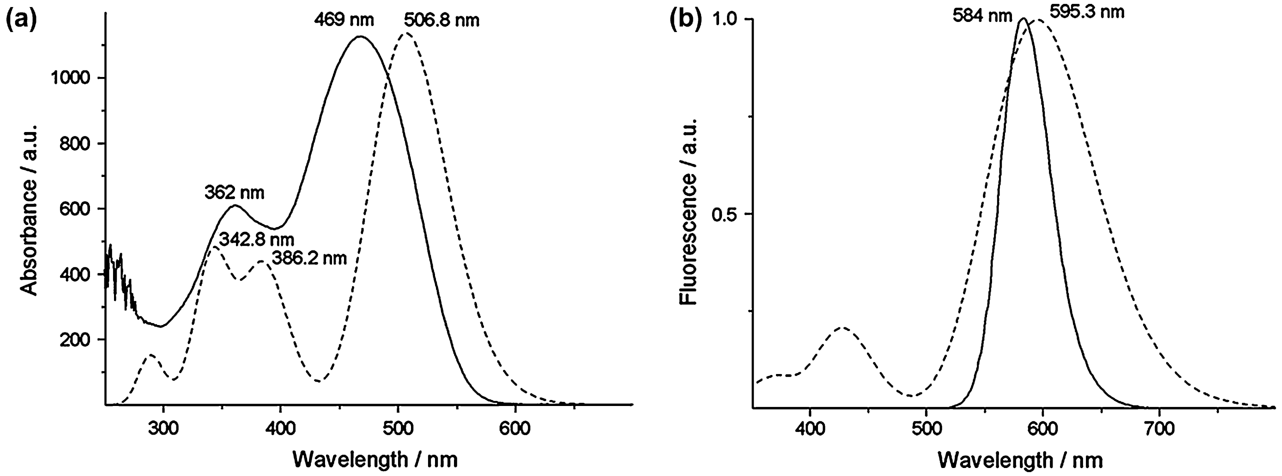


Fig. 2. The calculated (dashed lines) and experimental (solid lines) spectra of **1c** in $CHCl_3$. (a) Absorption; (b) fluorescence.

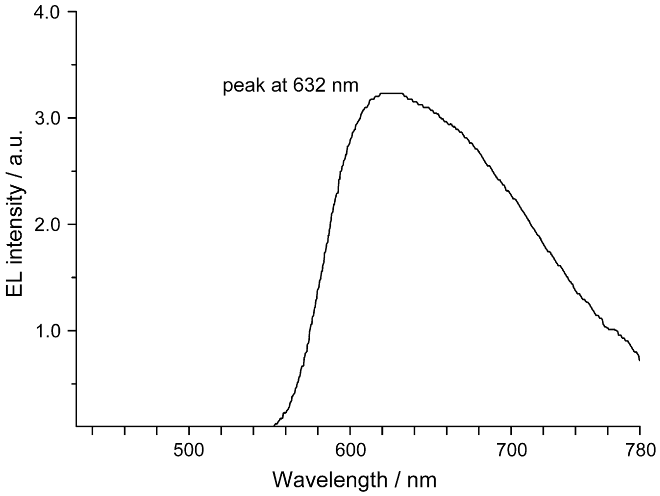


Fig. 3. EL spectra of red-emitting devices with the structure ITO/NPB/**1c**/Alq_3/LiF/Al.

showed saturated red emission at 632 nm (Commission Internationale de l'Eclairage (CIE) 1931 coordinates: $x = 0.71$, $y = 0.29$) (Fig. 3). The CIE coordinates of the device were comparable to those of devices using DCM analogs [7a]. Such significant red-shift in electroluminescence might be contributed to the more ordered aggregation in the double layer structures than in the solutions.

4. Conclusions

In summary, a series of PPV analogs with dicyanovinyl group as the electron acceptor were successfully developed through rational design assisted by the computational methods and organic synthesis. Subsequent fabricated EL devices using these compounds as dopants achieved saturated red emission. The CIE coordinates of the OLED were comparable to those of devices using DCM analogs. Our work has shown a way to modulate the emissions of the PPV-based EL devices to the red regions by reasonable modifications supported by the theoretical predications.

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