

Special Photophysical Properties of Poly(2,11-diquinoxalinopyrene)s*

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Abstract A diquinoxalinopyrene (**DQP**) derivative and the corresponding oligomers (**PDQPs**) with M_n of ca. 3300, 4200, 5600, and 7300 have been synthesized. It is found that the band gaps and highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels between **DQP** and its homopolymers only have a slight difference, implying a limited conjugation extension achieved from unimer to heptamer. The DFT calculation is in accordance with the experimental results. It reveals that the nodal planes are across the 2,11-positions in the LUMO and/or HOMO of **DQP**, dimer and trimer, which can be used to explain this special phenomenon.

Keywords Polydiquinoxalinopyrene; Photophysical properties; Nodal

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INTRODUCTION

Organic conjugated molecules and polymers are widely used in the field of optoelectronics, such as organic light-emitting diodes (OLEDs), phototransistors, organic photovoltaic cells (OPV), and organic field effect transistors (OFETs). Among them, polycyclic aromatic hydrocarbons (PAHs) or fused-ring containing compounds are of special importance for scientists. The extension of conjugated π -systems endows the molecules with not only reduced band gaps but also enhanced charge transporting mobility owing to more efficient intermolecular overlap and electronic coupling. For example, pentacene^[1–5], graphene nanoribbons^[6–10], azaacenes^[11–13], amorphous silicon^[14] and non-fullerene small molecule^[15] are intensively investigated for their special and outstanding opto-electronic properties. However, the stability and solubility of higher acenes ($n > 5$) gradually decrease, which limits their applications. The replacement of CH moieties with nitrogen atoms in PAHs has attracted increasing attention for improving both stability and solubility, *e.g.* diquinoxalinopyrene^[16–20] (**DQP**), apyrazine-containing^[21–23] acene-type molecular ribbon *etc.* have been intensively studied since Prof. Wang's group^[19] gave the promotion report.

DQP is a versatile mother core and can be further functionalized mainly *via* 3 ways: (1) Functionalize the quinoxaline moieties at 6,7,15,16-positions (*e.g.*, **I**, **II** and **III** in Scheme 1). McGrath *et al.*^[24] investigated the

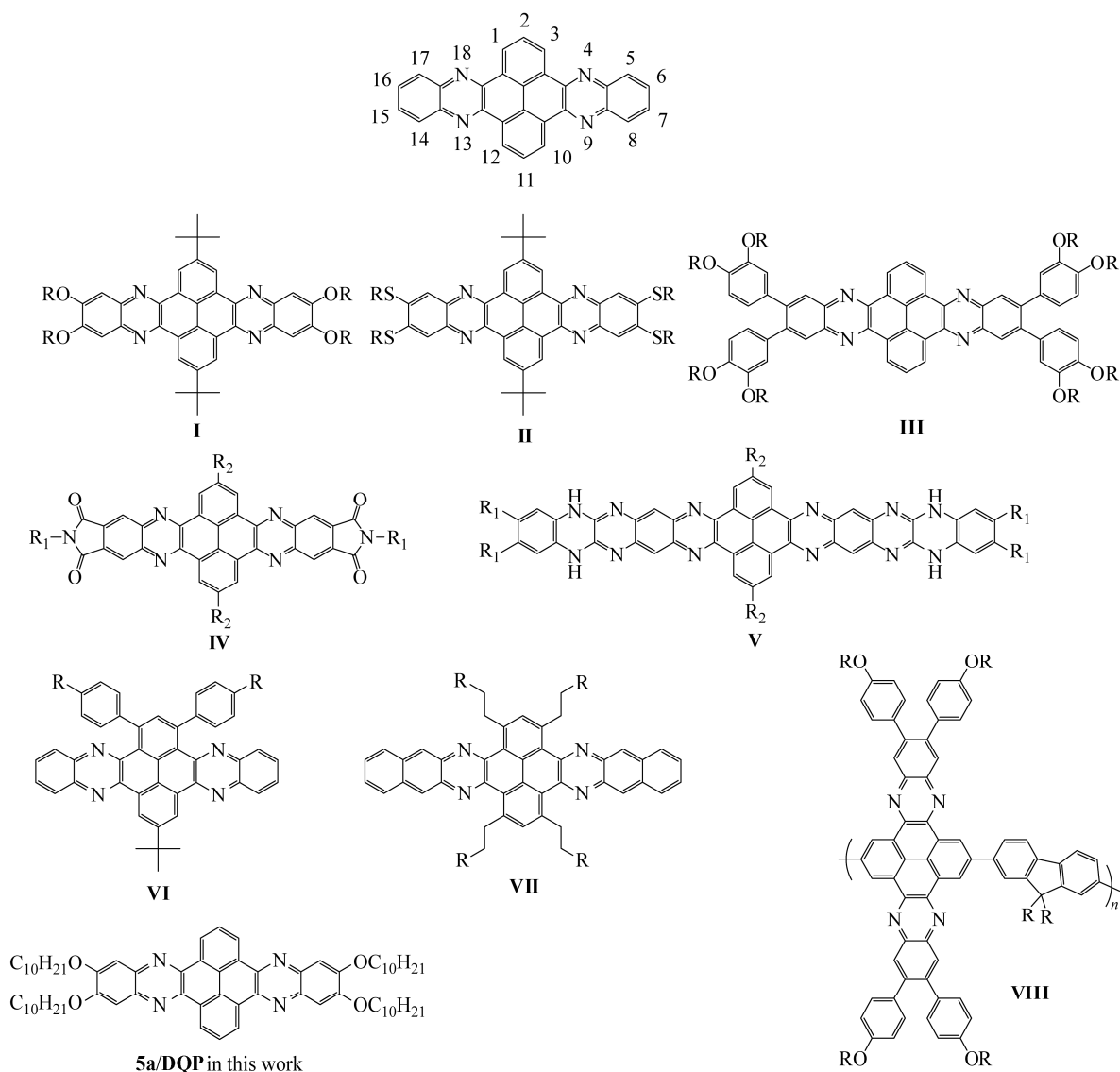
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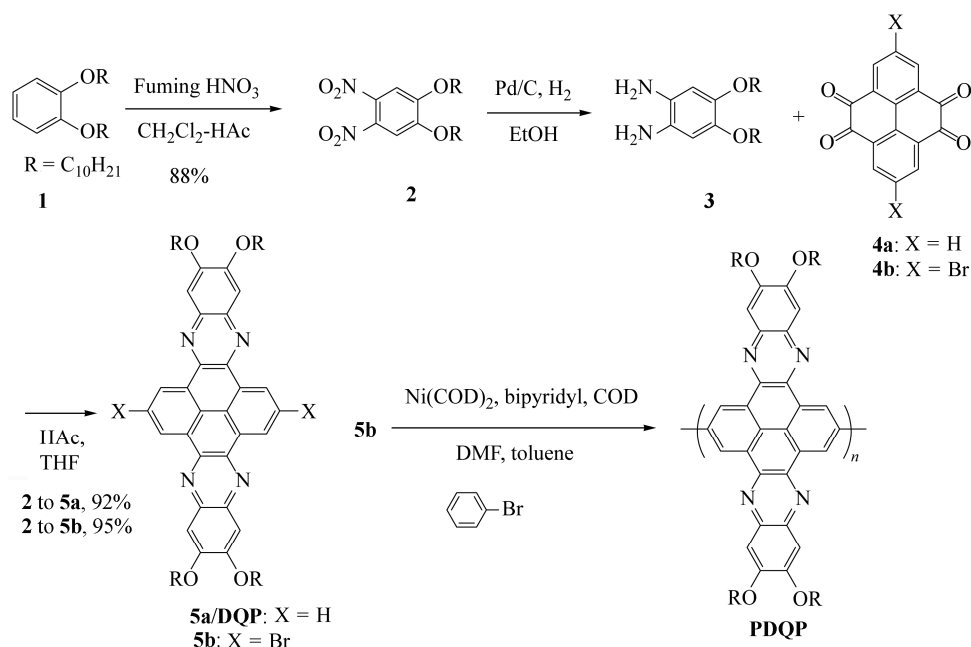


Scheme 1 The structures of **DQP** derivatives

substituent effect on the electronic properties and morphologies of compound **I**. Moustafa *et al.*^[25] reported some new **DQP** derivatives (**II**) with alkythio substituent at 6,7,15,16-positions on the quinoxaline moieties. Chen *et al.*^[26] introduced four phenyl groups with eight alkoxy chains in 6,7,15,16-positions of quinoxaline moieties (**III**) to increase the solubility. The solubility of **DQPs** can also be enhanced by end-capping triptycenyne^[27, 28]. More *et al.*^[29] introduced $-\text{CN}$ and $-\text{NO}_2$ groups to lower the LUMO level for increasing the stability of the final molecules. (2) Extend **DQPs** with more acenes structure on the quinoxaline moieties, *i.e.*, combining two or more pyrazine rings^[8] and thiadiazole rings^[30], attaching carboximide groups (**IV**)^[31] or further expanding quinoxaline to linear pyrazinacenes composed of both pyrazine and dihydropyrazine units (**V**)^[32]. (3) Functionalize pyrene moieties at 1,2,3,10,11,12-positions or/and 5,8,14,17-positions in **DQP** ring (*e.g.*, **VI** and **VII** in Scheme 1). Unlike the end groups at 6,7,15,16-positions, these substituents are close to the middle, and vertical or oblique to the long axis of pyrazine-pyrene-pyrazine ribbon. For example, silyl groups are introduced to 2,11-positions on pyrene moiety and other positions on quinoxaline moieties^[33, 34]. Zhang *et al.*^[35] reported two large pyrene-fused azaacenes: octaazadecacene (OADA) and tetraazaooctacene (TAOA) with silyl groups.

Lee *et al.*^[36–38] reported a series of T-shaped **DQPs** with different peripheral substitutions on one quinoxaline moiety. Feng *et al.*^[39] reported an efficient approach to 1,3-position functionalization of pyrene of **DQPs** (**VI**). Kulisic *et al.*^[32] expanded quinoxaline to benzoquinoxaline and introduced four substituents at 1,3,10,12-positions on the pyrene moieties to enhance the solubility (**VII**).

Although there are many reports referred to **DQP** molecules, the polymers connected with **DQP** molecules at 2,11-positions are rarely documented except a series of copolymers of **DQP** with fluorene (**VIII**)^[40]. It is well known that the conjugated polymers show significant different properties as compared with the corresponding unimers. Therefore, great efforts have been paid to explore the homopolymers of polydiquinoxalinopyrene (**PDQP**). In this paper, we report the synthesis of **PDQP** and its unique photophysical properties. In addition, the unimer of **5a/DQP** is also prepared (Schemes 1 and 2) for the purpose of comparison. It is found that the absorption onsets and HOMO/LUMO levels of **5a/DQP** and **PDQP** are very close. The absorption spectra of **PDQP** are nearly unchanged from M_n of ca. 3300 to ca. 7300, which means only a limited conjugation extension achieves from trimer to heptamer. DFT calculation is in accordance with the experimental results and can be used to explain this unique phenomenon.



Scheme 2 Synthetic route to **DQP** and **PDQP**

EXPERIMENTAL

General Information

All chemicals and reagents were used as received from Aldrich, TCI and Acros Chemical Co. unless specified otherwise. All solvents were carefully dried and purified before use. All manipulations involving air-sensitive reagents were performed under a dry argon atmosphere. ¹H-NMR spectra were measured on Varian Unity 400 or 600 MHz spectrometer using tetramethylsilane as an internal reference. ¹³C-NMR spectra were measured on Varian Unity 100 or 151 MHz spectrometer. C, H, N, S elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) and Br elemental content was analyzed by chemical titration. UV-Visible absorption spectra were recorded on a HP 8453 UV-Vis spectrophotometer. The photoluminescent (PL) spectra were obtained with a Fluorolog JY luminescence spectrometer. The fluorescent quantum yields of solution and films were measured in an integral sphere.

Compounds **4a**^[41] and **4b**^[40, 42, 43] in Scheme 2 were prepared according to the procedure reported in the literature.

1,2-Bis(3,7-dimethyloctyloxy)-4,5-dinitrobenzene (2)

To a stirred mixture of 5.740 g of **1** (14.719 mmol) in a mixed solution (100 mL of acetic acid and 100 mL of dichloromethane) was added dropwise 14.4 mL of HNO₃ (68 wt%) in 90 min in an ice-water bath. This mixture was warmed to room temperature and stirred for 2 h before cooling down to 0 °C again. Another 36.8 mL of fuming nitric acid was added in 3 h at 0 °C and the mixture was stirred for 40 h at room temperature. The reaction was quenched by pouring the mixture into 500 mL of ice-cold water and then extracted with methylene dichloride for 4 times. The combined organic layer was washed with brine, dried over K₂CO₃ and concentrated. The crude product was recrystallized from ethanol to afford 6.2 g of **2** as an orange solid (Yield: 93%). Anal. Calcd. for C₂₆H₄₄N₂O₆ (%): C, 64.97; H, 9.23; N, 5.83; O, 19.97; Found: C, 64.90; H, 9.22; N, 5.82. HRMS for C₂₆H₄₄N₂O₆ ESI *m/z* [M+Na]⁺, Calcd: 503.3092; Found: 503.3091. ¹H-NMR (600 MHz, CDCl₃, δ): 7.30 (s, 2H), 4.16–4.10 (m, 4H), 1.94–1.87 (m, 2H), 1.73–1.63 (m, 4H), 1.53 (dp, *J* = 13.3, 6.7 Hz, 2H), 1.39–1.12 (m, 12H), 0.96 (d, *J* = 6.4 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 12H). ¹³C-NMR (151 MHz, CDCl₃, δ): 151.80, 136.48, 107.82, 68.66, 39.18, 37.19, 35.61, 29.88, 27.98, 24.69, 22.69, 22.59, 19.61.

1,2-Bis(3,7-dimethyloctyloxy)-4,5-diaminobenzenes (3)

A mixture of 2.58 g of **2** (5.38 mmol) and 3.35 g of Pd/C (5 wt%) in 40 mL of ethanol was stirred at 40 °C overnight with bubbling hydrogen gas. The resulting mixture was filtered through Celite to remove the Pd/C catalyst. The filtrate containing **3** was transferred and stored under argon atmosphere and used without further purification.

6,7,15,16-Fourdecyloxy-diquinoxalino[2',3':4,5/9,10]pyrene (5a)

A mixture of pyrene (**4a**) (0.62 g, 1.48 mmol) and 10 mL of acetic acid in 150 mL of THF was refluxed for 10 min before **3** (the filtrate prepared above) was added. The mixture was refluxed overnight and cooled down. The solvent was stripped off under vacuum and 100 mL of water was added. The mixture was extracted with methylene dichloride for 4 times, washed with brine, dried over MgSO₄ and concentrated. The crude product was purified by silica column chromatography (eluent: petroleum:dichloromethane = 3:1, *V:V*) to afford 1.76 g of **5a** as a bright yellow powder (mp: 74–76 °C, total yield 92% from **2** to **5a**). Anal. Calcd. for C₆₈H₉₄N₄O₄ (%): C, 79.18; H, 9.19; N, 5.43; O, 6.20; Found: C, 79.11; H, 9.18; N, 5.42. HRMS for C₆₈H₉₄N₄O₄ ESI *m/z* [M+H]⁺, Calcd: 1031.7348; Found: 1031.7349. ¹H-NMR (600 MHz, CDCl₃, δ): 9.28 (d, *J* = 7.6 Hz, 4H), 7.92 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 4H), 4.21–4.12 (m, 8H), 1.96 (dd, *J* = 14.8, 7.4 Hz, 4H), 1.71 (dd, *J* = 13.7, 6.9 Hz, 8H), 1.51 (dt, *J* = 13.3, 6.6 Hz, 4H), 1.40–1.12 (m, 24H), 0.99 (d, *J* = 6.2 Hz, 12H), 0.84 (d, *J* = 6.6 Hz, 24H). ¹³C-NMR (151 MHz, CDCl₃, δ): 152.04, 138.58, 138.32, 128.20, 125.72, 124.56, 124.20, 105.34, 66.51, 38.33, 36.48, 34.95, 29.24, 27.03, 23.79, 21.75, 21.66, 18.82.

2,11-Dibromo-6,7,15,16-fourdecyloxy-diquinoxalino[2',3':4,5/9,10]pyrene (5b)

5b as a yellow powder (mp: 140–142 °C, total yield 95% from **2** to **5b**) was synthesized from **4b** and **3** according to the similar procedure used for preparation of **5a**. Anal. Calcd. for C₆₈H₉₂Br₂N₄O₄ (%): C, 68.67; H, 7.80; Br, 13.44; N, 4.71; O, 5.38; Found: C, 68.60; H, 7.79; Br, 13.40; N, 4.70. MALDI-TOF MS: Calculated for C₆₈H₉₂Br₂N₄O₄: 1189.3. Found: 1190.7. ¹H-NMR (400 MHz, CDCl₃, δ): 8.83 (s, 4H), 7.00 (s, 4H), 4.12 (m, 8H), 2.00–1.08 (m, 52H), 0.94 (d, 24H). ¹³C-NMR (100 MHz, CDCl₃, δ): 153.32, 139.39, 137.12, 129.63, 127.22, 122.28, 122.16, 105.85, 67.49, 39.40, 37.61, 36.03, 30.31, 28.08, 24.83, 22.80, 22.71, 19.83.

PDQP^[44–46]

In a Schlenk tube, bis(1,5-cyclooctadiene) nickel(0) (0.30 g, 1.1 mmol), 1,5-cyclooctadiene (0.12 g, 1.1 mmol), and 2,2'-bipyridine (0.17 g, 1.1 mmol) were dissolved in DMF (1.5 mL) and heated at 85 °C for 30 min under nitrogen atmosphere. A toluene solution (4.5 mL) of monomer **5b** (0.737 g, 0.62 mmol) was added, and the reaction mixture was heated at 85 °C for 12 h to 48 h and then bromobenzene (0.1 mL) was added to the mixture and stirred for 4 h. The mixture was poured into an equal volume mixture of methanol and acetone. The organic layer was extracted with toluene, washed with brine, and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude polymer was dissolved in a small amount of toluene and

precipitated twice from methanol. Then, the crude product was Soxhlet extracted with methanol, acetone and hexane to afford **PDQP** as a brown solid. Anal. Calcd. for $C_{68}H_{92}N_4O_4$ (%): C, 79.33; H, 9.01; N, 5.44; O, 6.22; Found: C, 79.28; H, 9.00; N, 5.43. $^1\text{H-NMR}$ (400 MHz, *o*-dichlorobenzene, δ): 10.0–9.5 (broad and weak, aromatic H), 7.5–7.0 (broad and weak, aromatic H), 4.5–4.0 (broad and weak, CH_2O —), 2.0–1.0 (strong, alkyl H).

RESULTS AND DISCUSSION

Synthesis

The synthetic route to **DQP** (**5a**) and **PDQP** is depicted in Scheme 2. Two branched long chains were chosen as the substituent to improve the solubility of the resulting **DQP** molecules with a large rigid planar structure. The first step is the alkylation of catechol with a long alkyl bromide to afford 1,2-bis(3,7-dimethyloctyloxy) benzene (**1**). Then, compound **1** was nitrated by fuming with nitric acid in a mixed solution of acetic acid and dichloromethane to obtain 1,2-bis(3,7-dimethyloctyloxy)-4,5-dinitrobenzene (**2**) in a high yield of over 90%. It is noteworthy that the yield of **2** is below 30% if single solvent is used, which may be due to the incomplete dissolution of the reactants. Subsequently, **2** was reduced with hydrogen gas in the presence of Pd/C to yield 1,2-bisalkoxy-4,5-diaminobenzenes (**3**). The diamine quickly changed colors from white to pink and to brown if exposed in air. It was used without further purification. We found this approach can afford **5** in a higher yield (> 90%) than that by using hydrazine hydrate as a reductant (*ca.* 30%–40%). This is because hydrazine hydrate may be stripped off before **3** reacting with pyrene-4,5,9,10-tetraone (**4a**)^[41]/2,7-dibromo-pyrene-4,5,9,10-tetraone (**4b**)^[40, 42, 43]. The excess hydrazine hydrate can also react with compound **4**, resulting in a low yield of **5** and time-consuming purification. As we mentioned above, **3** is very unstable and readily to be oxidized during the removal of excess hydrazine hydrate. In our case, we used hydrogen gas catalyzed with Pd/C as the reductant for **2**. The high yield by using this approach indicates that the Schiff-base formation from **3** and **4** is efficient. We also noticed that some insoluble polymers could be directly obtained from the diamine and pyrene-4,5,9,10-tetraone, the same as reported by others^[16–18, 47].

5a is a soluble **DQP** molecule. The optoelectronic properties of **5a** and its homopolymer of **PDQP** were compared. In order to obtain **PDQP**, **5b** with dibromo-functional groups was synthesized. After stirred at 85 °C for 2 days under typical Yamamoto reaction condition, **PDQP** with M_n of *ca.* 7300 (PDI = 1.38) was obtained. Indeed, it is not easy to get high molecular weight **PDQP** in a high yield, perhaps due to the low activity of the monomer. In our experiment, some oligomers with lower molecular weights were synthesized to clarify their special photophysical phenomena, which are demonstrated in the following part of this article. **PDQP** with lower molecular weights can be easily obtained by shortening the polymerization time (Table 1). The NMR spectra, HRMS or MALDI-TOF MS of all the compounds **2–5**, **DQP** and **PDQPs** are shown in Figs. S1–S13 (in supporting information, SI). No strong peak can be found at the aromatic region in the NMR spectrum of **PDQPs** although the aromatic peaks in **PDQP**-3300 show a little higher intensity than **PDQP**-7300. However, the peaks in NMR spectra of compounds **2–4** and unimer **DQP** can be easily assigned. The phenomena are similar to our previous observation^[48, 49], which may be due to the aggregation of the molecules with planar structures induced by strong π,π -stacking and interactions. The FTIR spectra all supported the structures of **PDQPs** (Fig. S14 in SI).

The degrees of polymerization (DPs) were calculated from MALDI-TOF using 2,5-dihydroxybenzoic acid as the matrix and the GPC chromatograms results (Figs. S15–S22 in SI). Unfortunately, the relative intensity of molecular ion decreases with increasing molecular weight, and no peak above 8.0×10^3 Da is observed. Thus, MALDI-TOF failed to give the full information of **PDQP**-7300 due to its relatively higher molecular weight. However, the difference can still be found between the spectra of **PDQP** oligomers. **PDQP**-3300 shows three main molecular ion peaks at 3092, 4214, 5247, corresponding to the trimer, tetramer, and pentamer, respectively. The tetramer content is the highest in **PDQP**-3300, which is accordance with the GPC result. **PDQP**-4200 shows the similar main mass fractions. However, some hexamer peaked at *ca.* 6185 appears. In the spectrum of

PDQP-5600, the hexamer content is the highest, and some heptamer and octamer peaks can be found. As mentioned above, the relative intensity of molecular ion signals decreases with increasing molecular weight. We suggest that the contents of heptamer and octamer might be much higher than those in the spectrum of **PDQP-5600**. It is not surprising that no strong peaks can be seen in the MALDI-TOF spectrum of **PDQP-7300** due to its high molecular weight. The results of MALDI-TOF measurement (Figs. S15–S18 in SI) for **PDQPs** are consistent with GPC outcomes (Figs. S19–S22 in SI).

Table 1 Synthesis and molecular weights of **PDQP** oligomers

Oligomer	Reaction time (h)	Yield (%)	$M_n \times 10^{-3}$ (Da)/ $M_w \times 10^{-3}$ (Da)	PDI	DP
PDQP-3300	12	15	3.3/4.7	1.41	3–5
PDQP-4200	24	19	4.2/6.6	1.56	3–6
PDQP-5600	36	22	5.6/8.3	1.48	5–7
PDQP-7300	48	25	7.3/10.0	1.38	7–9

Optical Properties of **DQP**

The optical properties of **DQP** were studied by means of UV-Vis absorption and photoluminescent (PL) spectroscopy. The absorption spectra of **DQP** in THF are shown in Fig. 1(a). It is clear that **DQP** has two absorption bands; one is in the range of 270–340 nm with a maximum at *ca.* 291 nm, and the other is in the range of 370–440 nm with two peaks at *ca.* 405 and 428 nm, respectively. **DQP** is a fused-ring compound, and it may aggregate at high concentrations. It is necessary to clarify the origination of the band in the range of 370–440 nm. We carefully recorded a series of the absorption spectra of **DQP** in THF by varying the concentrations as shown in Fig. 1(a). The results show that the absorbance of these two bands decreases spontaneously when the concentrations reduce from 10 $\mu\text{mol/L}$ to 0.1 $\mu\text{mol/L}$. We confirm such a result by using chloroform as an alternative solvent, as shown in Fig. 1(b). It is evidenced that the bands in the range of 370–440 nm originate not from excimer but due to the π - π^* transition of the overall conjugated compound. The absorption onset of **DQP** in solution is always at 440 nm, indicating that the conjugation length remains nearly unchanged in the concentrations ranging from 10 $\mu\text{mol/L}$ to 0.1 $\mu\text{mol/L}$. However, the **DQP** film shows obvious red-shift as compared with its solution, which may be due to the inter-molecule aggregation in the solid state.

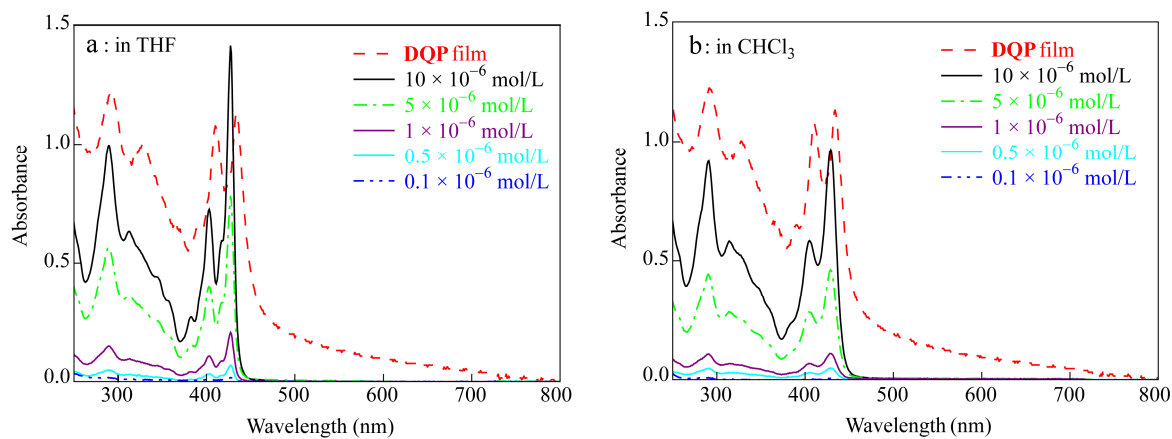


Fig. 1 Absorption spectra of **DQP** in THF (a) and chloroform (b)

As reported, pyrene in dilute solution has two major absorption bands with maximum absorption wavelengths at about 274 and 336 nm, respectively^[50]. As **DQP** contains a pyrene core, the two discontinuous absorption bands in **DQP** spectra may be related to the two absorption bands of pyrene. The red-shift from pyrene to **DQP** may be due to the extension of conjugation along the quinoxaline-pyrene-quinoxaline axis. Li's group also reported that pyrene fused perylene diimides showed much wider absorption range than perylene

diimides with the substituent of pyrene^[51].

Pyrene derivatives are well-studied optoelectronic chromophores, which have been widely used for fluorescent probes and biological labeling^[52, 53]. Pyrene is a rare solvatochromic molecule that shows the dependence of absorption and/or emission spectral shifts on the dielectric and dipolar properties of their local environment (solvents). We found that the photoluminescent spectra of **DQP** in THF (as shown in Fig. 2a) were apparently different from those in chloroform (as shown in Fig. 2b). The former has clear vibrational fine structures while the latter seems featureless. However, further study is needed to clarify the mechanism on these phenomena.

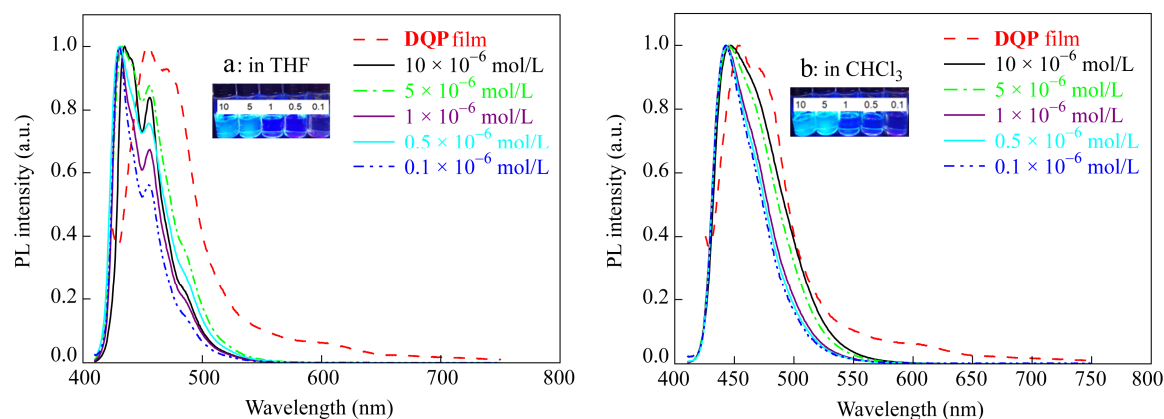


Fig. 2 PL spectra of **DQP** in THF (a) and chloroform (b) (The inset pictures are photographs under 365 nm UV excitation. The online version is colorful.)

Optical Properties of PDQP with M_n of ca. 7300

The absorption spectra of **PDQP** with M_n of ca. 7300 (**PDQP**-7300) are shown in Fig. 3(a). The absorption spectra of **DQP** are also given in Fig. 3(a) for comparison and all of the optical parameters are summarized in Table 2. **PDQP**-7300 shows two broad absorption bands of 270–370 nm and 370–460 nm, which are very close to those of **DQP**.

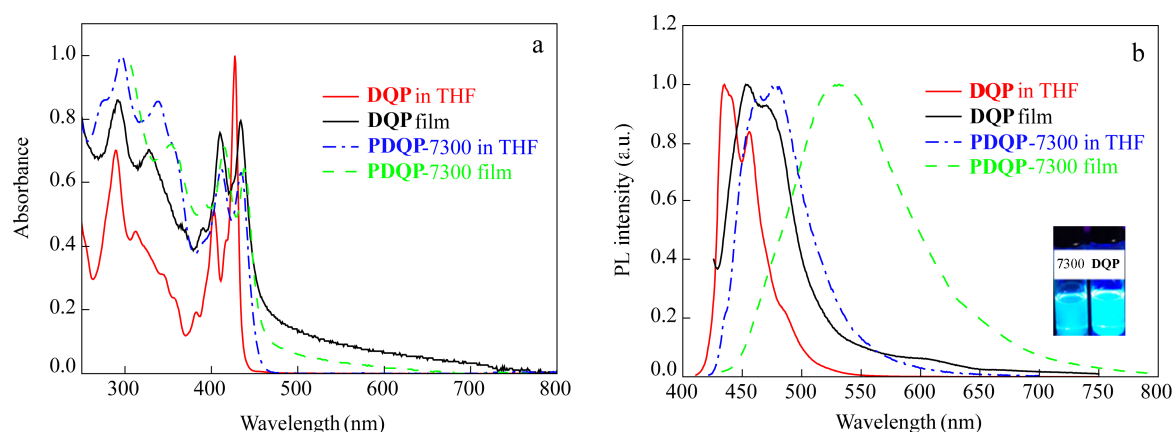


Fig. 3 The absorption (a) and PL (b) spectra of **DQP** and **PDQP**-7300 (**PDQP** with M_n of ca. 7300) (The inset picture is the photograph of **DQP** and **PDQP**-7300 solution under 365 nm UV excitation. The online version is colorful.)

The absorption onsets of **PDQP**-7300 in THF are red-shifted 20 nm as compared with those of **DQP**, which means the decrease in the band gap is only 0.16 eV after polymerization. Remarkably, the absorption onsets of **PDQP**-7300 and **DQP** film are much closer, indicating nearly no difference after the inter-molecular aggregation

in the solid state. This is a rare example for the conjugated polymers. Generally, the conjugated polymers show significant conjugation extension when compared with the corresponding monomers or unimers.

The difference between **DQP** and **PDQP-7300** can be easily found from their PL spectra (Fig. 3b). **PDQP-7300** in THF (20 $\mu\text{mol/L}$) shows a PL emission maximum at 460 nm with a shoulder at 480 nm. The THF solution of **DQP** (10 $\mu\text{mol/L}$) slightly red-shifts 5–6 nm, while the **DQP** film exhibits larger red-shift of *ca.* 18 nm. The emission maximum of **PDQP** film bathochromically shifts to *ca.* 534 nm due to the inter-chain aggregation, which is a common phenomenon in the PL spectra of conjugation polymers.

Table 2 Opto-physical properties and DFT calculation of **DQPs** and **PDQP** oligomers

Compd.	$\lambda_{\text{Abs,max}}^a$ (nm)	$\lambda_{\text{Abs,onset}}^b$ (nm)	$\lambda_{\text{PL,max}}^c$ (nm)	$E_{\text{ox,onset}}$ (V)	Experimental (eV)			DFT (eV)			QY (%)
					HOMO	LUMO	E_g	HOMO	LUMO	E_g	
DQP in THF	289, 312; 383, 427	440	435, 456				2.82				22.9
DQP film	291, 326; 390, 434	460	453, 473	1.54	−5.94	−3.24	2.70	−6.066	−2.647	3.420	1.1
d-DQP								−5.987	−2.633	3.353	
t-DQP								−5.839	−2.621	3.218	
PDQP-7300 in THF	296, 338; 390, 434	460	461, 479				2.70				7.3
PDQP-7300 film	302, 354; 413, 438	462	528	1.48	−5.88	−3.20	2.68				2.6
PDQP-5600 in THF	296, 338; 390, 434	460	461, 478				2.70				6.7
PDQP-5600 film	299, 340; 412, 438	462	529	1.50	−5.90	−3.22	2.68				3.5
PDQP-4200 in THF	296, 339; 390, 435	460	462, 478				2.70				6.6
PDQP-4200 film	300, 339; 413, 437	463	519	1.51	−5.91	−3.23	2.68				2.2
PDQP-3300 in THF	296, 338; 390, 434	460	461, 475				2.70				8.5
PDQP-3300 film	298, 337; 412, 438	463	498	1.52	−5.92	−3.24	2.68				3.8

^a The wavelength of maximum absorption in absorption spectra; ^b The wavelength of absorption edge in absorption spectra;

^c The wavelength of maximum emission in PL spectra

Optical Properties of Other **PDQP** Oligomers

We prepared a series of **PDQP** oligomers with lower molecular weights to confirm the rarely reported phenomenon of close absorption onsets of **PDQP-7300** and **DQP**. The detailed synthetic procedure can be found in the first part of the discussion section.

The absorption spectra of **PDQP** oligomers in THF solution are shown in Fig. 4. The absorption spectra were measured in a dilute solution in order to avoid the influence of film morphology and intermolecular aggregation. It is clear that the difference between unimer **DQP** and **PDQP** oligomers is larger than that between **PDQP** oligomers with various M_n or DPs. The absorption peaks and onsets of **PDQP** oligomers in THF bathochromically shift by 10–20 nm as compared with those of **DQP**. Furthermore, the shapes of the peaks are different. The absorption band and peak of **DQP** at *ca.* 310–355 nm and *ca.* 400 nm increase significantly after polymerization. However, the absorption spectra of **PDQP** oligomers (DP = 3–8) are nearly identical except the slight increase of the shoulder at *ca.* 340 nm with increasing M_n . These results also confirm the special phenomenon above mentioned.

Although the absorption onsets of **PDQP** oligomers in THF are red-shifted by 20 nm as compared with those of **DQP**, the optical band gaps decrease only *ca.* 0.16 eV after polymerization. Generally, the conjugated polymers have much smaller band gaps than the corresponding unimers. For example, poly(2,7-phenanthrylene)s exhibit the band gaps of 2.84–3.08 eV^[54] but *ca.* 3.55 eV for phenanthrylene^[55]. We find another example

similar to **DQP**, which is the well-studied pyrene. It was reported that the absorption onsets of poly(2,7-pyrene)s were close to pyrene due to the nodal properties of their frontier orbitals^[56]. In our case, **PDQP-3300** shows the same band gap as **PDQP-7300**, which indicates that the conjugation extension of **PDQP** has ground to a halt when the DP is above 3.

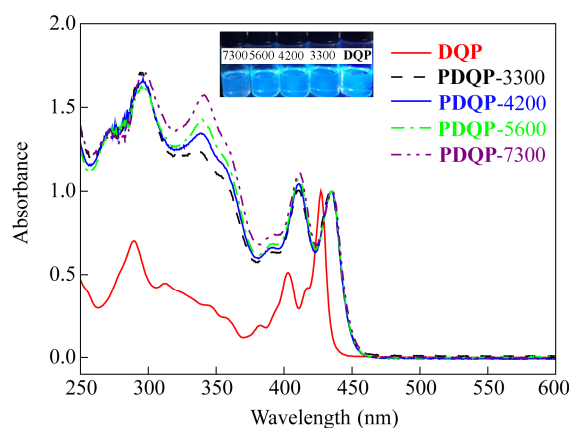


Fig. 4 The absorption spectra of **DQP** and **PDQPs** in THF (The inset pictures are photographs of **DQP** and **PDQPs** in solution under 365 nm UV excitation. The online version is colorful.)

The absorption spectra of **PDQPs** film are shown in Fig. S23 (in SI). It can be found that the **PDQP** oligomers have the similar absorption onsets. The PL spectra of **PDQPs** solution and film are given in Fig. S24 (in SI). Although the **PDQPs** solution emits blue light under UV excitation (inset pictures in Fig. 4), the fluorescent peaks display significant bathochromic shift in solid films due to the aggregation. The photophysical parameters including UV, PL maxima and quantum yield (QY) are summarized in Table 2.

Electrochemical Properties

Electrochemical properties of **DQP** and **PDQPs** films were evaluated by means of cyclic voltammetry (CV), which was carried out on a Potentiostat/Galvanostat Model 283 (Princeton Applied Research Co.) in a solution of tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) (0.1 mol/L) and acetonitrile with a scanning rate of 100 mV/s at room temperature. It is found that these materials display irreversible oxidation peaks in a relatively high potential range as shown in Fig. 5. The onsets of the oxidation peaks are located at *ca.* 1.54 V for **DQP** and 1.48 V versus $\text{Hg}/\text{Hg}_2\text{Cl}_2$ for **PDQP-7300**. Hence, the highest occupied molecular orbital (HOMO) energy

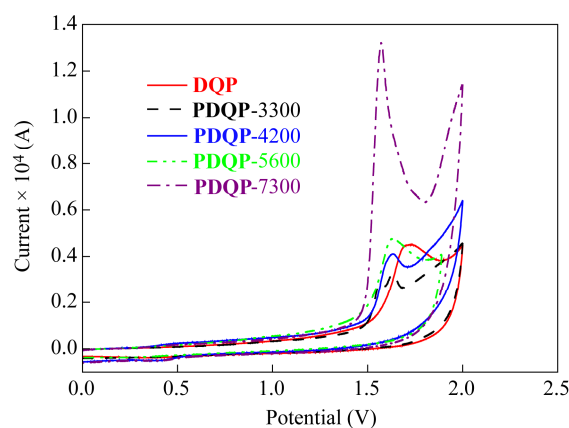


Fig. 5 CV curves of **DQP** and **PDQPs**

values are estimated to be -5.94 eV for **DQP** and -5.88 eV for **PDQP-7300** according to the empirical formula, $E_{\text{HOMO}} = -(E_{\text{ox, onset}} + 4.4)^{[57]}$. It is not surprising that **PDQP-7300** has higher HOMO level than **DQP** due to the reduced band gap. However, it is unusual that the unimer and polymer have such close HOMO levels. Together with their optical band gaps, the LUMO energy levels are calculated to be -3.24 eV for **DQP** and -3.20 eV for **PDQP-7300**. **PDQP-4200** and **PDQP-5600** exhibit the oxidation potential slightly higher than **PDQP-7300** but lower than **DQP**. The oxidation onset and HOMO/LUMO levels are summarized in Table 2. The DFT calculation was carried out to understand why the unimer and the homopolymer have the similar energy levels.

DFT Calculations

The optimization of all geometries was carried out by the density functional theory (DFT) calculation at the B3LYP/6-31G(d) level, and the energies were obtained at B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) by using the Gaussian 03 program^[58] which was successfully applied in our previous studies^[59–62]. **PDQP** is replaced by the dimer and trimer of **DQP**, noted as d-**DQP** and t-**DQP**, because it is impossible to calculate the polymers. Furthermore, all the alkyl groups are simplified as methyl groups to save the computation time. The optimized geometry and frontier molecular orbitals of HOMO and LUMO for **DQP**, d-**DQP** and t-**DQP** are displayed in Fig. 6 and the energy levels are summarized in Table 2.

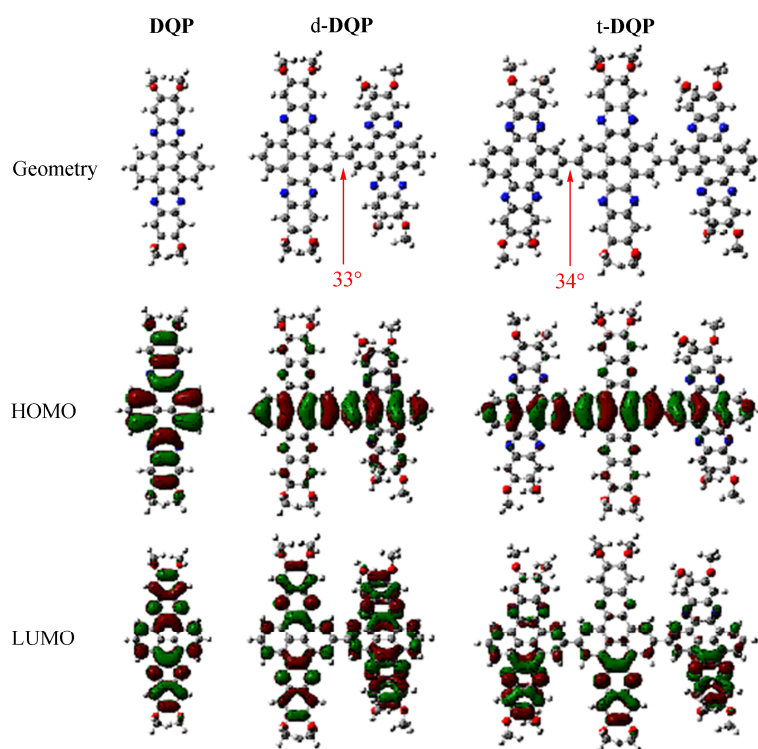


Fig. 6 DFT calculation of **DQP**, d-**DQP** and t-**DQP**

DQP exhibits a fully planar geometry. The HOMO and LUMO of **DQP** locate symmetrically on the conjugated core with a nodal plane across the 2,11-positions, which is similar to that of pyrene unit^[63, 64]. However, d-**DQP** and t-**DQP** are different. Firstly, moderate dihedral angles (33° – 34°) appear between the **DQP** planes although these planes remain planar after coupling. Secondly, the HOMOs of d-**DQP** and t-**DQP** are mainly delocalized along the central biphenyls, which is totally different from that of **DQP**. The LUMOs are a bit complicated. The LUMO of d-**DQP** is quite similar to that of **DQP**, but it is only delocalized on half of **DQP** repeating units in t-**DQP** according to the calculation results. However, the nodal plane across the 2,11-positions in the LUMOs of all these model compounds can still be found, which means that the conjugation extension

influences the LUMO levels of **PDQP** after polymerization.

The calculated HOMO and LUMO energy levels are listed in Table 2. The calculated results (especially the HOMO levels) are quite close to the experimental data. In addition, **DQPs** also show close values of HOMO/LUMO levels and band gaps. It is known that the energy gap between HOMO and LUMO of conjugated polymers presents a linear relationship to the reciprocal of polymerization degree^[65], implying that the polymers have reduced band gaps with increasing DP, and the largest band gap reduction appears from unimer **DQP** to d-**DQP** and t-**DQP**. However, DFT results show that the band gap reduction value from **DQP** to t-**DQP** is only 0.202 eV, very close to the experimental result (0.16 eV). We speculate that the nodal plane across the 2,11-positions in the LUMO and/or HOMO of **DQP** and **PDQPs** may be responsible for this special phenomenon. Similar results are reported earlier that pyrene and its dimer and trimer have very close absorption maximum and first reduction potentials, attributed to the nodal plane across the 2,7-positions of pyrene, and resulting in electronic decoupling phenomenon of pyrene compounds^[66].

CONCLUSIONS

A diquinoxalinopyrene derivative and its homopolymer were synthesized in a high yield. The absorption spectra show that their main difference is the high-energy band in the range of 270–340 nm. Nevertheless, their absorption onsets are very close. The HOMO/LUMO levels are also very close according to the cyclic voltammetry measurement. The DFT calculation results support the experiment data. It reveals the nodal plane across the 2,11-positions in the LUMO and/or HOMO of **DQP** and **PDQPs**, which may be responsible for this special phenomenon. The experimental results verify the effect of nodal properties and offer another way to get polymers without significant conjugation extension.

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