Supplementary Material (ESI) for Chemical Communications

Supporting information

Conjugated Alternating Copolymers Containing Both Donor and Acceptor Moieties in the Main Chain

Ming Zhang, Changduk Yang, Wojciech Pisula[+], Ashok K. Mishra, Gang Zhou, Bruno Schmaltz, Martin Baumgarten and Klaus Müllen*

Max-Planck-Institutt for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany.

[+]Present address: Degussa AG, Process Technology & Engineering, Process Technology – New Processes, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang, Germany

*Corresponding author. E-mail: muellen@mpip-mainz.mpg.de

I. Experimental section

1. General Methods:

Chemicals were obtained from Fluka, Aldrich, and Merck and used as received if not specified otherwise. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker DPX 250 and Bruker 300 AMX spectrometers. Field Desorption (FD) mass spectra were obtained on a VG Instruments ZAB 2-SEFPD. Elemental analysis was carried out on a Foss Heraeus Vario EL in the Institute for Organic Chemistry at the Johannes Gutenberg University, Mainz. The optical absorption measurements were performed at ambient temperature using an UV/Vis/NIR Perkin-Elmer Lambda 900 spectrometer. The PL measurements were performed on a J&M TIDAS spectrofluorometer. Gel permeation chromatography (GPC) analysis was performed with PL gel columns (10^3 and 10^4 Å pore widths) connected to an UV/vis detector. The calibration was based on poly-*para*-phenylene standards with narrow weight distribution.

2. The measurement of the 2D-WAXS

The 2D-WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a 2D Siemens detector. A double graphite monochromator for the Cu-K_α radiation (λ=0.154 nm) was used. The samples were prepared by mechanical alignment by using a home-build extruder at a temperature of 180 °C, at which both compounds become plastically deformable. The experiments were performed only at room temperature, since no structure change at higher temperature or after annealing was observed.

3. Synthesis

3.1 LPPK Monomer

Pentaphenylene diketone diboronate ester (2):

A solution of monomer **1** (500 mg, 0.47 mmol), bis(pinacolato)diboron (286 mg, 1.1 mmol), $PdCl_2(dppf)$ (80 mg, 0.01 mmol), and KOAc (276 mg, 2.82 mmol) in degassed 1,4-dioxane (22 ml) was stirred at 80 °C overnight. The reaction was quenched by adding water, and the resulting mixture was washed with ethyl acetate (30 ml × 3). The organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to yield dark red solid. The solid was purified by silica gel chromatography by 3 % ethyl acetate in hexane to give the desired compound (**2**) as a dark yield solid (400 mg, 74 %). FD-MS: m/z = 1159.6 (calcd. 1159.28). ^1H NMR (250 MHz, CD_2Cl_2): δ 8.01 (s, 2H), 7.86 (s, 2H), 7.78 (m, 6H), 7.61 (s, 2H), 2.12 (t, J = 8Hz, 7.75Hz, 8H), 1.37 (s, 24H), 1.06 (m, 40H), 0.81-063 (m, 20H). ^{13}C NMR (62.90 MHz, CD_2Cl_2): δ 192.90, 160.64, 150.48, 146.68, 144.09, 143.24, 140.68, 134.39, 129.37, 119.89, 116.57, 116.12, 84.42, 56.47, 40.72, 32.32, 30.48, 29.74, 25.324, 24.39, 23.15, 14.38.

3.2 Carbazole Monomer

2-bromo-7-chloro-9H-carbazole (3b)

1). A mixture of 1, 4-dibromo-2-nitrobenzene (50.0 g, 0.18 mol), 1-chloro-4-iodobenzene (59.7 g, 0.25 mol) and copper powder (-140 mesh) (34.0 g, 0.53 mol) was heated at 195°C with stirring for 15 h. The reaction mixture was cooled to ambient temperature, and then hot toluene (400 ml) was added. Unreacted copper powder and insoluble materials were filtered off. The filtrate was washed with a saturated NaCl solution and dried over $MgSO_4$, and the solvent was removed in vacuo. The obtained residue was purified by column chromatography on silica gel with Hexane/Ethyl acetate (5/1) as the eluent to give 4-bromo-4'-chloro-2-nitrobiphenyl as a yellowish powder (40.6 g, 73 %). ^1H-NMR (250 MHz, CD_2Cl_2) δ_H 8.05 (d, 1H, J = 1.9Hz), 7.79 (d d, 1H, J = 2.0Hz, J = 8.2Hz), 7.43 (d, 2H, J = 8.5Hz), 7.32 (d, 1H, J = 8.3Hz), 7.25 (d, 2H, J = 8.5Hz). ^{13}C

NMR (62.90 MHz, CD_2Cl_2) δ 149.81, 136.22, 135.65, 135.21, 134.62, 133.80, 129.80, 129.50, 127.79, 122.25. Anal. Calcd. for $C_{12}H_7BrClNO_2$: C, 46.11; H, 2.26; N, 4.48. Found: C, 46.06; H, 2.34; N, 4.57.

2) A 250 ml flask was charged with 25.0 g (80.0 mmol) of 4-bromo-4'-chloro-2-nitrobiphenyl and 140 ml of triethylphosphite. The resulting mixture was refluxed under Argon for 20 h. The excess of triethylphosphite was removed under reduced pressure and the crude product was washed with dichloromethane. The residue was purified by column chromatography on silica gel with Hexane/Ethyl acetate (4/1) as eluent to give 2-bromo-7-chloro-9H-carbazole as white solid (11.2 g, 50%). ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.27 (s, 1H) 7.97 (d, 1H, J = 8.4Hz), 7.91 (d, 1H, J = 8.3Hz), 7.63 (d, 1H, J = 1.4Hz), 7.47 (d, 1H, J = 1.6Hz), 7.36 (d d, 1H, J = 1.6Hz, J = 8.3Hz), 7.22 (d d, 1H, J = 1.7Hz, J = 8.4Hz). ^{13}C NMR (75.46 MHz, CD_2Cl_2): δ= 141.17, 140.72, 132.41, 123.69, 122.29, 122.02, 121.96, 121.75, 121.03, 120.04, 114.44, 111.47. FD-MS: m/z 281.1 (calcd: 280.5).

4-(2,7-dibromocarbazol-9-yl)benzoic acid methylester (4a):

3a (1 g, 3.08mmol) was dissolved in anhyd. DMF (15 ml) and NaH (148 mg, 3.7 mmol, 60 % in oil) were added. After 30 min stirring at room temperature p-fluorobenzoicacidmethylester (0.6 ml, 4.62 mmol) was added and the reaction mixture was stirred for 3 days at 70 ºC under Argon. The reaction was cooled, extracted with DCM and washed with water. The organic fraction was dried with $MgSO_4$, the solvent removed in vacuo and the product recrystallized from DMF. (White solid, 917 mg, 65 %) FD-MS: m/z = 458.5 (calcd. 459.14). ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.37 (d, J = 8.52Hz, 2H), 8.21 (d, J = 8.2Hz, 2H), 7.86 (d, J = 8.52Hz, 2H), 7.62 (d, J = 1.27Hz, 2H), 7.51 (d d, J = 8.2Hz, J = 1.57 Hz, 2H), 3.98 (s, 3H), ^{13}C-NMR (75.46 MHz, CD_2Cl_2): δ 166.29, 142.46, 141.49, 132.43, 130.96, 127.72, 124.92, 123.10, 122.66, 120.89, 113.85, 52.43. Element analysis (%) $C_{20}H_{13}Br_2NO_2$: Calcd.: C, 52.32; H, 2.85; N, 3.05. Found: C, 52.21; H, 2.93; N, 3.14.

4-(2-bromo-7-chlorocarbazol-9-yl)benzoic acid methylester (4b):

(White solid, 60 %) FD-MS: m/z = 414.8 (calcd. 412.98) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.31 (d, J= 8.25Hz, 2H), 8.05 (d d, J = 8.25Hz, J = 8.25 Hz, 2H), 7.65 (d, J = 8.52Hz, 2H), 7.57 (s, 1H), 7.46 (d, J= 1.5Hz, 1H), 7.415 (s, 1H), 7.32 (d d, J = 8.25Hz, J = 1.75Hz, 1H), 3.98 (s, 3H), ^{13}C-NMR (62.90 MHz, CD_2Cl_2): δ 166.66, 142.09, 141.70, 141.07, 132.82, 132.07, 130.35, 127.15, 124.55, 123.10, 122.13, 121.87, 120.47, 113.60, 110.67, 52.86.

[4-(2,7-dibromo-carbazol-9-yl)-phenyl]-bis-(4-octyloxy-phenyl)-methanol (5a):

4-Octyloxybromobenzene (2.73 g, 9.58 mmol) was dissolved in anhyd. THF (15 ml) and cooled to -78ºC. **4a** (2 g, 4.35 mmol) in 50 ml anhyd. THF was added under cooling to this mixture. The reaction mixture was stirred over night, extracted with DCM and washed with water. The organic fraction was dried with $MgSO_4$, the solvent removed in vacuo and the product purified by column chromatography using 5 % ethyl acetate in hexane. (White solid, 2.52 g. 70 %). FD-MS: m/z = 841.3 (calcd. 839.76) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 7.99 (d, J = 8.2Hz, 2H), 7.56 (m, 4H), 7.41 (m, 4H), 7.26 (d, J = 8.85Hz, 4H), 6.90 (d, J = 8.85Hz, 4H), 3.97 (t, J = 6.62Hz, 4H, OCH_2), 2.89 (s, 1H, OH), 1.74 (m, 4H, CH_2), 1.30 (m, 20H, Alkyl), 0.88 (t, J = 6.95Hz, 6H, CH3). ^{13}C-NMR (75.46 MHz, CD_2Cl_2): δ 158.92, 148.14, 142.27, 139.28, 135.44, 130.01, 129.44, 126.54, 123.92, 122.11, 121.87, 120.24, 114.22, 113.49, 81.57, 68.50, 32.21, 29.75, 29.67, 29.63, 26.42, 23.04, 14.24. Element analysis (%) $C_{47}H_{53}Br_2NO_3$, Calcd.: C, 67.22; H, 6.36; N, 1.67. Found: C, 68.09, H, 6.20; N, 1.63.

[4-(2-bromo-7-chlorocarbazol-9-yl)-phenyl]-bis-(4-octyloxyphenyl)methanol (5b):

(Colourless oil, 72 %) Fd-MS: m/z = 793.5 (calcd. 795.3) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.01 (d d, J = 8.25Hz, J = 8.25Hz, 2H), 7.59 (m, 3H), 7.45 (m, 4H), 7.29 (m, 5H), 6.92 (d, J = 8.25Hz, 4H), 3.99 (t, J = 6.5Hz, 4H, OCH_2), 2.91 (s, 1H, OH), 1.78 (m, 4H, CH_2), 1.31 (m, 20H, Alkyl), 0.88 (t, J = 7Hz, 6H, CH_3). ^{13}C-NMR (62.90 MHz, CD_2Cl_2): δ 159.08, 148.28, 142.53, 142.15, 139.50, 135.62, 132.64, 130.21, 129.68, 126.62, 124.19, 122.28, 122.01, 121.92, 121.76, 121.44, 120.34, 114.41, 113.64, 110.73, 81.77, 68.66, 32.45, 26.99, 29.88, 26.66, 23.29, 14.52.

4-{[4-(2,7-dibromocarbazol-9-yl)-phenyl]-bis-(4-octyloxyphenyl)methyl}-phenyl (6a): 5a (1.5 g, 1.78 mmol) and acetylchloride (3 ml, 37.4 mmol) were refluxed for 24 h. The acetylchloride was distilled off and the remaining solid was careful dried. Phenol (1.84 g, 19.6 mmol) was added to this solid and the mixture was stirred for 3 days at 120ºC. The phenyl was distilled off (kugelrohr) and the product purified by column chromatography using 5 % ethyl acetate in hexane. (Off-white solid, 1.07 g, 66 %). FD-MS: m/z = 915.3 (calcd. 915.86). ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 7.98 (d, J = 8.45Hz, 2H), 7.57 (s, 2H), 7.44 (m, 6H), 7.17 (m, 6H), 6.84 (d, J = 9Hz, 6H), 4.9 (s, 1H, OH), 3.95 (t, J = 6.57Hz, 4H, OCH_2), 1.77 (m, 20H, Alkyl). ^{13}C-NMR (75.46 MHz, CD_2Cl_2): δ 157.74, 154.47, 148.41, 142.25, 139.26, 135.51, 134.25, 133.06, 132.59, 132.35, 125.95, 123.90, 122.08, 121.84, 120.21, 114.69, 113.72, 113.51, 81.57, 68.50, 32.31, 29.68, 29.65, 26.43, 23.04, 14.27. Element analysis (%) $C_{53}H_{57}Br_2NO_2$, Calcd.: C, 69.51; H, 6.27; N, 1.53. Found: C, 69.55; H, 6.09; N, 1.45.

4-{[4-(2-bromo-7-chlorocarbazol-9-yl)-phenyl]-bis-(4-octyloxyphenyl)methyl}phenyl (6b): (yellow oil, 60 %) FD-MS: m/z= 870.7 (calcd. 869.3) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.04 (d d, J = 8.25Hz, J = 8.5Hz, 2H), 7.58 (d, J = 1.5, 1H), 7.47 (m, 6H), 7.28 (m, 1H), 7.17 (m, 6H), 6.85 (m, 6H), 4.89 (s, 1H, OH), 3.98 (t, J = 5Hz, 4H OCH_2), 1.78 (m, 4H, CH_2), 1.31 (m, 20H, Alkyl), 0.88 (t, J = 7Hz, 6H, CH3). 1.78 (m, 4H, CH_2), 1.31(m, 20H, Alkyl), 0.88 (t, J = 7Hz, 6H, CH_3). ^{13}C-NMR (62.90 MHz, CD_2Cl_2): δ 157.91, 154.45, 148.517, 142.57, 142.18, 139.86, 139.42, 134.47, 133.22, 132.79, 132.53, 126.12, 124.06, 122.27, 122.00, 121.90, 121.74, 121.37, 120.27, 114.87, 113.90, 110.76, 32.41, 30.27, 29.95, 29.90, 29.84, 26.64, 23.24, 14.46

2,7-dibromo-9- {4-[tris- (4-octyloxyphenyl)methyl]phenyl}carbazole (7a):

6a (400 mg, 0.43 mmol) was dissolved in THF (7 ml). KOH (1Pellet) and octylbromide (0.084 ml, 0.48 mmol) were added under Argon and the reaction mixture was refluxed for 18 h. The reaction was cooled, extracted with DCM and washed with water. The organic fraction was dried with $MgSO_4$, the solvent removed in vacuo and the product purified by column chromatography using 5 % ethyl acetate in hexane. (White solid, 427 mg, 95 %). Fd-Ms.: m/z = 1030.0 (calcd. 1028.07). ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 7.99 (d, J = 5.97Hz, 2H), 7.57 (s, 2H), 7.42 (m, 6H), 7.17 (d, J = 6.92Hz, 6H), 6.84 (d, J = 6.57Hz, 6H), 3.95 (t, J = 6.27Hz, 6H, OCH_2), 1.77 (m, 6H, CH_2), 1.30 (m, 30H, Alkyl), 0.88 (t, J = 5.97Hz, 9H, CH_3). ^{13}C-NMR (75.46 MHz, CD_2Cl_2): δ 157.73, 154.47, 148.46, 142.26, 139.30, 134.23, 133.06, 132.34, 125.96, 123.90, 121.84, 120.20, 113.72, 113.70, 113.51, 68.38, 63.26, 32.22, 29.75, 29.71, 29.63, 26.45, 23.04, 14.24. Element analysis (%) $C_{61}H_{73}Br_2NO_3$, Calcd.: C, 71.27; H, 7.16; N, 1.36. Found: C, 71.82; H, 7.10; N, 1.27.

2-bromo-7-chloro-9-{4-[tris-(4-octyloxyphenyl)methyl]phenyl}carbazole (7b):

(White solid, 95 %). Fd-Ms.: m/z = 982.8 (Calcd. 981.5) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.03 (d d, J = 8.25Hz, J = 8.5Hz, 2H), 7.59 (s, 1H), 7.49 (m, 6H), 7.28 (d d, J = 8.25Hz, J = 1.5Hz, 1H), 7.19 (d, J = 8.75Hz, 6H), 6.85 (d, J = 8.75Hz, 6H), 3.98 (t, J = 6.5Hz, 6H, OCH_2), 1.80 (m, 6H, CH_2), 1.31 (m, 30H, Alkyl), 0.88 (t, J = 4Hz, 9H, CH_3). ^{13}C-NMR

(62.90 MHz, CD_2Cl_2): δ 157.90, 148.60, 142.57, 142.19, 139.48, 134.43, 133.23, 132.59, 132.53, 126.11, 124.05, 122.27, 122.00, 121.90, 121.74, 121.37, 120.27, 113.88, 113.68, 110.78, 68.55, 63.43, 32.41, 29.96, 29.91, 29.84, 26.64, 23.25, 14.46.

Carbazole monomer 8:

2 (150 mg, 0.13 mmol) and **7b** (280 mg, 0.312 mmol) and K_2CO_3 (2 ml, 1 M) were dissolved in 5 ml THF in a 50 ml Schlenk flask. The solution was purged with Argon for 30 minutes, and then tetrakis(triphenylphosphine)palladium was added and the reaction was stirred at 80 ºC overnight. The reaction was cooled, extracted with DCM and washed with water. The organic fraction was dried with $MgSO_4$, the solvent removed in vacuo and the product purified by column chromatography using 3 % ethyl acetate in hexane. (Dark red solid, 210 mg, 60 %). FD-MS.: m/z = 2711.2 (calcd. 2712.7) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.01 (s, 2H), 7.86 (s, 2H), 7.42 (m, 6H), 7.78 (t, J = 3Hz, 6H), 7.61 (s, 2H), 2.12 (t, J = 8Hz, 8H, CH_2), 1.37 (s, 24H, CH_3), 1.06 (m, 40H, Alkyl), 0.88-0.61 (m, 20H). ^{13}C-NMR (75.46 MHz, CD_2Cl_2): δ 192.956, 160.27, 157.95, 152.07, 148.30, 146.70, 143.70, 143.10, 142.64, 142.44, 142.12, 140.70, 140.54, 139.66, 139.59, 135.04, 134.52, 133.21, 132.58, 132.24, 127.42, 126.23, 122.64, 122.54, 122.36, 121.76, 121.09, 120.86, 116.22, 116.04, 113.91, 110.70, 109.11, 68.61, 63.49, 56.62, 40.85, 32.43, 32.32, 30.53, 30.28, 29.98, 29.85, 29.76, 29.71, 26.68, 24.49, 23.25, 23.16, 14.44, 14.37.

3.3 Alternating D-A copolymer

Synthesis of P1: 2 (113 mg, 0.0973 mmol) and **7a** (100 mg, 0.0973 mmol), K_2CO_3 (2 ml, 2 M) and 1 drop of aliquat 336 were dissolved in 3 ml toluene and 1ml water in a 50 ml Schlenk flask. The solution was purged with Argon for 30 minutes, and then tetrakis(triphenylphosphine)palladium was added and the reaction was stirred at 80 ºC for 3 days. Then a toluene solution of phenyl boronate eater was added followed by the addition of bromobenzene and stirred overnight. The resulting mixture was poured into a mixture of methanol and concentrated hydrochloric acid (2:1) and stirred overnight. The precipitated dark solid was redissolved in THF and added dropwise to methanol (200 ml). The resulting solid was filtered off and subjected to Soxhlet extraction for 2 days in acetone. The residue was then redissolved in THF and precipitated again from methanol, filtered, washed with methanol, and dried. (120 mg, 56 % yield) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.30-6.86 (m, 34H), 3.96 (m, 6H, OCH_2), 2.13-0.77 (m, 113H, Alkyl). GPC analysis: M_n=1.0×10^4 g/mol, M_w= 1.3×10^4, and D=1.3 (against PPP standard).

Synthesis of P2: Bis(cyclooctadiene)nickel (2.4 equiv), cyclooctadiene (2.4 equiv), and 2,2′-bipyridine (2.4 equiv) were dissolved in dry toluene (3.5 ml) and dry N,N-dimethylformamide (3.5 ml) in a Schlenk within a glovebox. The mixture was heated as 60 ºC with stirring under Argon for 30 minutes to generate the catalyst, and then a solution of the monomer **8** (230 mg, 0.085 mmol) in dry toluene (7 ml) was added. The reaction was heated to 75 ºC for 2 days. After a bromobenzene toluene solution was added and stirred overnight, the resulting mixture was poured into a mixture of methanol and concentrated hydrochloric acid (2:1) and stirred overnight. The precipitated dark solid was redissolved in THF and added dropwise to methanol (200 ml). The resulting solid was filtered off and subjected to Soxhlet extraction for 2 days in acetone. The residue was then redissolved in THF and precipitated again from methanol, filtered, washed with methanol, and dried. (200 mg, 87 %) ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 8.35-6.75 (m, 564H), 3.95 (m, 12H, OCH_2), 2.18-0.85 (m, 158H, Alkyl). GPC (M_n) of GPC analysis: M_n= 4.4×10^4 g/mol, M_w= 8.4×10^4, and D= 1.9 (against PPP standard). P2 Calcd. C, 83.86; H, 7.71; N, 1.04; Found. C, 84.58; H, 8.48; N, 0.96;

II. UV/vis absorption and PL spectra of P1

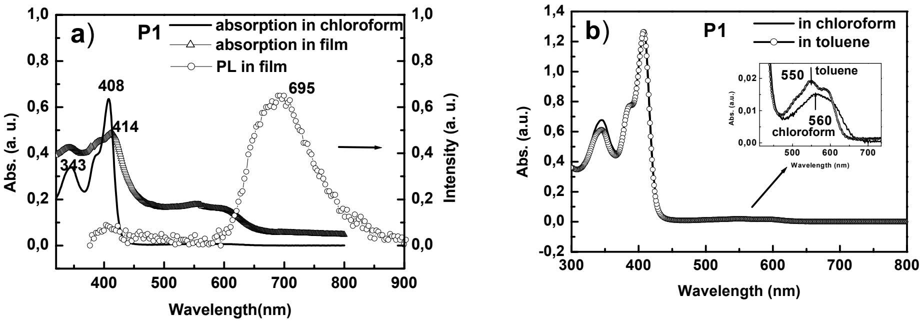

Fig. 1 a) UV/vis absorption and PL spectra of **P1** in a dilute chloroform solution and drop-casted film on quartz glass (excitated at 320 nm); b) absorption spectra of **P1** in different solvents.

Fig. 1 shows the UV/vis absorption and photoluminescence spectra of **P1** in a dilute chloroform solution and a drop-casted film on quartz glass at room temperature, together with the absorption spectra in different solvents. **P1** showed the similar opticalphysics properties as **P2**, two absorption maxima at around 343 nm and 408 nm in solution, the effect of the solvent polarity (Fig. 1 (b)), and the absorption spectra of thin films were apparently broader, red-shifted and the absorption intensity at 550 nm is stronger compared with that of **P1** in solution. The PL of **P1** in solution was very week, while that of drop-casted films was stronger, as shown in Fig.1 (a), excitated at 320 nm. The emission spectra of **P1** showed only one maximum at 695 nm.

III. UV/vis absorption and PL spectra of the pentaphenylene diketone (LPPK)

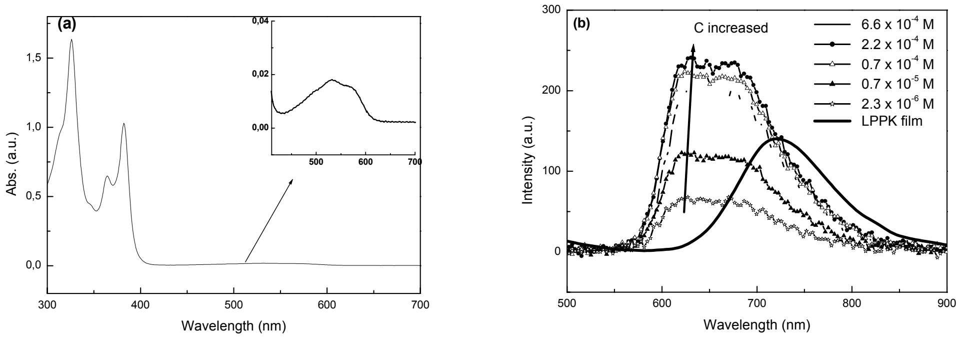

Fig. 2 (a) UV/vis absorption of pentaphenylene diketone **(LPPK)** in a dilute chloroform solution; (b) PL spectra of **LPPK** with different concentration in THF and drop-casting film

Fig. 2(a) is the UV/vis absorption of pentaphenylene diketone **(LPPK)** in a dilute chloroform solution. A weak absorption band at 550 nm corresponding to the n-π* transition in the caybonyl of **LPPK** can be found, which supports the assign of the absorption of the copolymers. Fig. 2(b) are the PL spectra of the pentaphenylene diketone monomer **2** at different concentrations in THF solution and a drop-casted film. It can be seen that with the increasing concentration (from 2.3×10^{-6} M to 6.6×10^{-4} M in THF), the peak shifted from 620 nm to 633 nm in THF solution. While in the solid state, the emission peak is at around 720 nm, which should be due to the stacking. Compared the pentaphenylene diketone monomer emission in solid state with that of the D-A block copolymer **P1** and **P2**, the pentaphenylene diketone emission is more red-shifted. This is because of the introduction of the carbazole units, and their “huge” side chain make the stacking weaker.

Fig. 3 shows the PL spectra of **P2** and **LPPK** at the same concentration (2.8×10^{-4} M). When the P2 has the same concentration as the pure monomer LPPK, stronger emission quenching of P2 was found, which supports the existence of a charge separated state upon photoexcitation. Different concentrations were also tested and gave the same results. These results suggest the donor-acceptor copolymers **P1** and **P2** to be good candidates for photovoltaic devices.

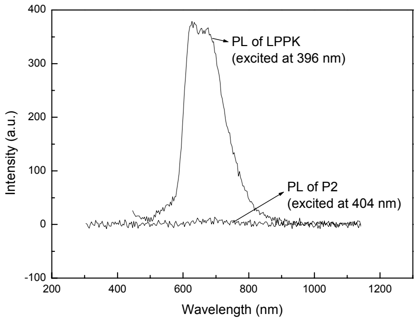

Fig. 3 The PL spectra of P2 and LPPK at the same concentration (2.8×10^{-4} M)