Supporting Information

Effect of Band Gap Alignment on the Hole Transport from Semiconducting Block Copolymers to Quantum Dots

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1. Chemicals and Instrumentation

Chemicals. Unless mentioned otherwise, all chemicals were used as purchased. Pentafluorophenol was obtained from Fluorochem (UK). Anhydrous N,N'-Dimethyl formamide was obtained from Sigma Aldrich and stored over activated molecular sieves (4 Å).2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from diethyl ether and stored at -18 °C. Anhydrous THF and dioxane were freshly distilled from sodium. Dithiobenzoic acid benzyl ester was synthesized as previously reported.¹ It was purified by column chromatography with chloroform as eluent. Pentaflourophenyl acrylate (PFPA)² and Vinyl-TPD monomer³ were synthesized as described in the literature. Methanol was dried over Mg and distilled afterwards. Toluene was distilled from calcium hydride. DMF was freshly distilled from calcium hydride and not exposed to light. CdO (99.9%), zinc oxide (ZnO, \geq 99.0%), oleic acid (OA, 90%), myristic acid (My,99 %), 1-octadecene (1-ODE, 90%), n-trioctylphosphine (TOP, 90%), 1-dodecanethiol (DDT, 97%), zinc acetate dehydrate (Zn(Ac)₂·2H₂O, > 98%), were purchased from Sigma-Aldrich. Potassium hydroxide (KOH, GR reagent) was obtained from Duksan Phrmaceutical Co. Ltd.

Instrumentation. All ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz FT NMR spectrometer. All ¹⁹F NMR spectra were recorded on a Bruker 400 MHz FT NMR spectrometer. Chemical shifts (δ) are given in parts per million relative to TMS. Samples were prepared in deuterated solvents and their signals referenced to residual nondeuterated solvent signals. The polymers' molecular weight was determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as solvent and with the following parts: pump PU 1580, auto sampler AS1555, UV detector UV 1575 (detection at 254 nm), RI detector RI 1530 from JASCO. Columns were used from MZ-Analysentechnik: MZ-Gel SDplus 10.2 Å and MZ-Gel SDplus 10.6 Å. Calibration was done using polystyrene standards purchased from Polymer Standard Services. IR spectra were recorded on Perkin-Elmer 100 FTIR spectrometer using an ATR unit. UV-Vis spectra were recorded using a Jasco V-630 spectrophotometer (1 cm x 1 cm quartz cell). Emission spectra were taken with a PGSTAT30 from Autolab (Metrohm) in o-dichlorobenzene with tetrabutyl ammonium tetrafluoroboride as conductive salt. Ag/AgCl with saturated LiCl in ethanol was used as reference electrode, graphit as counter electrode and platin as working electrode. The scan rate was 0.01 V/s and the step potential 0.00244 V. The current–voltage–luminance characteristics were measured using a Keithley 236 source-measure unit and a Keithley 2000 multimeter coupled with a calibrated Si photodiode. Electroluminescence spectra of the QLEDs were obtained using a Konica-Minolta CS-1000A spectroradiometer.

1. Synthesis of 2-methyldisulfanyl-ethylamine



2-Methyldisulfanyl-ethylamine was synthesized in a slightly different way than according to literature.⁴ 5.00 g cysteamine hydrochloride (44.0 mmol, 1 eq) were dissolved in 30 mL of dry methanol in a nitrogen atmosphere and cooled to 0 $^{\circ}$ C while stirring. 4.63 g methyl methanethiosulfonate (36.7 mmol, 1.2 eq) was dissolved in 20 mL of dry methanol was added dropwise. The solution was stirred for 16 h at room temperature. The solvent was removed in vacuum and the residual oil was dissolved in 5 mL of dry dichloromethane. It was then washed three times with 5 N sodium bicarbonate and one time with water. After drying with magnesium sulfate and evaporating the solvent, 2.56 g (20.8 mmol, 47%) of the product were obtained as slightly yellow oil.

¹H NMR: (CDCl₃, 300 MHz) δ [ppm] = 1.30 (s, 2 H, -NH₂), 2.34 (s, 3 H, -CH₃), 2.71 (t, 2 H, -S-CH₂- J1 = 6.3 Hz, J2 = 6.07 Hz), 2.95 (t, 2 H, H₂N-CH₂-, J1 = 6.2 Hz, J2 = 6.1 Hz).

2. Synthesis of the monomer vinyl-TPDF



Scheme S 2. Synthesis of the monomer in three steps. a) Tris(dibenzylidenacetone)dipalladium(0), 1,1'-Bis-(diphenylphosphino)-ferrocene, NaO'Bu, Toluol, 12 h, 90 °C. b) POCl₃, DMF, 24 h, 80 °C c) MePh₃PBr, KO'Bu, 24 h, r.t.

Synthesis of N,N'-Bis(4-trifluoromethyl phenyl)-N,N'-bisphenyl-1,1'-bisphenyl-4,4'-diamine (TPDF) via Buchwald-Hartwig coupling

2.18 g tris(dibenzylideneacetone)dipalladium(0) (2.38 mmol, 0.04 eq) and 3.10 g 1,1'-bis-(diphenylphosphino)ferrocene (5.60 mmol, 0.08 eq) were dissolved in 50 mL of anhydrous toluene in a nitrogen atmosphere. Oxygen was removed with two freeze-pump-thaw cycles. 29.43 g 4-bromobenzotrifluorid (130.78 mmol, 2.2 eq), 20 g N,N'-diphenylbenzidine (59.44 mmol, 1 eq) and 17.14 g sodium tert-butoxid (178.32 mmol, 3 eq) were dispersed in 250 mL of dry toluene. The mixture was degassed with one freeze-thaw-pump cycle. The catalyst solution was added via a canula and the resulting mixture was degassed again The flask was immersed in a hot oil bath (90 °C) and stirred over night. 250 mL of methanol were added to quench the reaction and the crude product was extracted with water/diethyl ether. After evaporation of the solvent, the product was purified via column chromatography (silica gel, hexanes:ethyl acetate 10:1, $R_f = 0.5$). 24.63 g (39.4 mmol, 66%) TPDF were obtained as a light yellow powder.

¹H NMR (CDCl₃, 300 MHz) δ [ppm] = 7.09-7.17 (m, 14 H), 7.29-7.34 (m, 4 H), 7.41-7.50 (m, 8 H).

¹³C NMR (CDCl₃, 75 MHz) δ [ppm] = 121.42, 122.7, 122.89, 123.33, 124.43, 125.38, 125.62, 126.36, 127.79, 129.69, 135.96, 146.00, 146.73, 150.75.

FD-MS [m/z] calcd. for C₃₈H₂₆F₆N₂ 624.20; found 623.37 (100.00%), 624.36 (48.05%), 625.35 (8.57%), 626.34 (1.25%).

Synthesis of N,N'-2-bis(4-trifluoromethyl phenyl)-N-phenyl-N'-4-formylphenyl(1,12-biphenyl)-4,4-diamine (aldehyde-TPDF)

24.63 g TPDF (39.4 mmol, 1 eq) were dissolved in 110 mL of anhydrous DMF in a nitrogen atmosphere in a Schlenk tube and cooled down to 0 °C in an ice bath. 15.10 g phosphoroxychlorid (98.5 mmol, 2.5 eq) were added dropwise over 20 minutes. The solution was stirred for 20 more minutes at 0 °C and then immersed into a warm oil bath (50 °C). The oil bath was then heated up to 80 °C and the reaction was stirred over night. It was then poured into a 1.2 N sodium acetate solution (1000 mL) and stirred for 30 minutes. The crude product was

collected by filtration, washed with water and dried at high vacuum. It was then purified by column chromatography (silica gel, hexanes:dichloromethane 1:1, Rf = 0.4). The starting material (9.00 g, 14.4 mmol, 37%) could be recovered as well for repeating the reaction ($R_f = 0.7$). 10.00 g aldehyde-TPDF (15.3 mmol, 39%) were obtained as yellow powder.

¹H NMR (CDCl₃, 300 MHz) δ [ppm] = 7.09-7.34 (m, 15 H), 7.42-7.57 (m, 8 H), 7.75 (d, 2 H, J = 8.8 Hz), 9.86 (s, 1H, -CHO).

¹³C NMR (CDCl₃, 75 MHz) δ [ppm] = 121.59, 122.32, 122.65, 123.01, 123.44, 124.34, 124.53, 125.23, 125.67, 126.35, 126.77, 127.91, 128.22, 129.72, 130.70, 131.40, 135.43, 137.74, 144.77, 146.36, 146.66, 149.46, 150.68, 152.36, 190.48.

FD MS [m/z] calcd. for $C_{39}H_{26}F_6N_2O$ 652.19; found 651.25 (100.00%), 652.25 (45.64%), 653.25 (8.31%).

Synthesis of N,N'-2-bis(4-trifluoromethyl phenyl)-N-phenyl-N'-4-vinylphenyl(1,12-biphenyl)-4,4-diamine (vinyl-TPDF)

23.38 g Methyltriphosphonium bromide (62.1 mmol, 3 eq) and 7.34 g potassium tert-butoxide (62.1 mmol, 3 eq) were dissolved in 400 mL anhydrous THF in a nitrogen atmosphere, cooled to 0 °C and allowed to react for 90 minutes. 13.15 g Aldehyde-TPDF (20.7 mmol, 1 eq) were dissolved in 87 mL anhydrous THF in a nitrogen atmosphere and added quickly dropwise to the yellow suspension. The reaction mixture was stirred for 16 hours at room temperature. It was then cooled to 0 °C again and 220 mL 10% HCl were added carefully. The product was extracted with chloroform/saturated sodium hyrogencarbonate and finally washed with water. The combined organic phases were dried with magnesium sulfate and the solvent was removed under reduced pressure. By column chromatography (silica gel, hexanes:dichloromethane 1:1, $R_f = 0.8$), 11.51 g vinyl-TPDF (17.7 mmol, 85%) were obtained as a white powder.

¹H NMR (CDCl₃, 300 MHz) δ [ppm] = 5.21 (d, 1 H, Htrans, J = 11.7 Hz), 5.68 (d, 1 H, Hcis, J = 18.4 Hz), 6.68 (dd, 1 H, 4J = 17.6 Hz Htrans, 10.9 Hz Hcis), 7.08-7.17 (m, 12 H), 7.28-7.36 (m, 4 H), 7.41-7.50 (m, 7 H).

¹³C NMR (CDCl₃, 75 MHz) δ [ppm] = 113.26, 121.42, 122.90, 123.15, 123.34, 123.58, 124.43, 125.20, 125.36, 125.45, 125.61, 126.37, 127.45, 127.79, 129.69, 133.63, 136.00, 145.80, 146.03, 146.26, 146.73, 150.52, 150.75.

FD-MS [m/z] calcd. for C₄₀H₂₈F₆N₂ 650.22; found 649.34 (100.00%), 650.32 (37.58%), 651.34 (8.35%).

Anal. calcd. for C₃₈H₂₆F₆N₂ [%] C 73.84, H 4.34, N 4.31; found C 73.75, H 4.45, N 4.04.

3. Synthesis of the homopolymers

4.00 g Vinyl-TPDF (6.2 mmol, 120 eq), 12.5 mg dithiobenzoic acid benzyl ester (0.05 mmol, 1 eq) and 0.8 mg 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.005 mmol, 0.1 eq) were dissolved in 7 mL of anhydrous dioxane in a Schlenk tube and equipped with a stirring bar. Oxygen was removed with four freeze-pump-thaw cycles and the flask was immersed into a hot oil bath (80 °C). After stirring for 48 hours, the polymer was precipitated in methanol. The precipitate was collected, redissolved in a few milliliters of anhydrous THF and precipitated in methanol again. This was repeated two more times. The polymer was dried in a 10 mbar vacuum at 40 °C for 12 hours. P2 was obtained as yellow powder, 1.68 g (42%). GPC: $M_n = 12,600$ g/mol, $M_w = 13,900$, PDI: 1.10. ¹H NMR (CDCl₃, 300 MHz) δ [ppm] = 1.72-2.31 (br, 3H), 6.62 (br, 2H), 6.94 (br, 11H), 7.16 (br, 6H), 7.29 (br, 3H). ¹⁹F NMR (CDCl₃, 376 MHz) \Box [ppm] = -62.08 (br).

RAFT-polymerization of P1. The polymerization was carried out under the same conditions as for vinyl-TPDF. P1: GPC: $M_n = 15,000$ g/mol, $M_w = 15,800$, PDI: 1.05.

4. Synthesis of the block copolymers

As an example, the synthesis of **BCP2** is explained. **BCP1** was synthesized in the same way. 780 mg **P2** (0.06 mmol, 1 eq), 590 mg PFPA (2.5 mmol, 40 eq) and 1 mg AIBN (0.006 mmol, 0.1 eq) were dissolved in 5 mL anhydrous dioxane in a Schlenk tube and equipped with a stirring bar. Oxygen was removed by four freeze-pump-thaw cycles and the flask was immersed into a hot oil bath (80 °C). After stirring for 48 hours, the polymer was precipitated in methanol. The precipitate was collected, redissolved in a 10 mbar vacuum at 40 °C for 12 hours. **BCP2** was obtained as yellow powder, 880 mg (42%). GPC: $M_n = 13,800$ g/mol, $M_w = 14,800$, PDI: 1.09. ¹⁹F NMR (CDCl₃, 376 MHz) δ [ppm] = -162.43 (br), -157.09 (br), -153.60 (br), -62.08 (br). FT-IR [cm⁻¹]. 2923, 1785 (-CO-O-), 1604, 1518 (Ar-F), 1493, 1320, 1113, 1068, 823. BCP1: GPC: $M_n = 16,300$ g/mol, $M_w = 17,500$, PDI: 1.07. ¹⁹F NMR (CDCl₃, 376 MHz) δ [ppm] = -162.49 (br), -158.27 (br), -153.35 (br). FT-IR [cm⁻¹]. 2928, 1783 (-CO-O-), 1594, 1522 (Ar-F), 1489, 1238, 1002, 818.

5. Polymer analog reaction

500 mg BCP2 (0.04 mmol, 1 eq) were dissolved in 5 mL anhydrous THF in nitrogen atmosphere. 246 mg 2-methyldisulfanyl-ethylamine (2 mmol, 60 eq) and 200 mg triethylamine (2 mmol, 60 eq) were added. The resulting solution was stirred at 40 °C for 20 hours and then precipitated in methanol. After collecting by centrifugation, the polymer was precipitated three more times in methanol to give 450 mg poly(TPDF-b-SSMe) as a white powder. FT-IR [cm⁻¹]. 2922, 1598 (-CO-NH-), 1495, 1313, 1266, 1164, 1113, 1066, 818, 694. ¹⁹F NMR: no signal. Poly(TPD-b-SSMe): FT-IR [cm⁻¹]. 2922, 1604 (-CO-NH-), 1489, 1238, 1036, 820, 694. ¹⁹F NMR: no signal.

6. Preparation of QD-conducting polymer hybrids

QD-poly(TPD-b-SSMe) or QD-poly(TPDF-b-SSMe) hybrid solution was prepared by mixing 0.40 mL of QD dispersion (13 wt% in toluene) with 0.40 mL of conducting polymer solution (5 wt% in toluene). The mixture was immersed in a sonication bath for 20 minutes and then purified by precipitation/redispersion method. The hybrid was precipitated with excess ethanol and redispersed in toluene. After 10 cycles of the purification process the precipitates were redispersed in 1.7 mL of anhydrous toluene (40 mg/mL) and kept in a refrigerator.

7. Device fabrication and characterization

QD-conducting polymer hybrid devices were fabricated on patterned ITO glass substrates, cleaned with isopropanol, acetone, and methanol in an ultrasonic bath. Firstly, 20 mg/mL of the ZnO solution was spun on a patterned ITO substrate at 2000 rpm for 60 sec and baked in N_2 atmosphere at 90 °C for 30 min. The resulting film thickness was 45 nm. Then, 40 nm thick layers of QD-conducting polymer hybrid films were deposited by spin-casting at 3000 rpm for 30 sec. Finally, TCTA (60 nm), MoO₃ (10 nm), and Al (100 nm) were sequentially evaporated with a deposition rate of 0.5–1 Å sec⁻¹, 0.2 Å sec⁻¹, and 3–5 Å sec⁻¹ respectively.

8. Cyclovoltammetry



Figure S 1. Cyclovoltammetry of P1 (left) and P2 (right) in o-dichlorobenzene.

The HOMO and LUMO level were calculated via the following equations:

$$HOMO = -(4.4 + P_{ox})eV$$
 (eq. 1)

$$LUMO = HOMO + E_g \tag{eq. 2}$$

$$E_g = \frac{1240}{\lambda_{onset}} \tag{eq. 3}$$

The formal potential of the ferrocene/ferrocenium couple was 0.5 V versus the Ag/AgCl electrode. λ_{onset} was determined from the UV-Vis spectra.

9. GPC



10. Synthesis of CdSe/CdS/CdZnS/CdZnS red QDs

Prior to the synthesis of QDs, zinc oleate $(Zn(OA)_2)$, cadmium oleate $(Cd(OA)_2)$, TOPSe, and TOPS were prepared as shell-forming precursors. For the $Cd(OA)_2$, 5 mmol of CdO, 5 mL of OA, and 5 mL of 1-ODE were loaded in a 50 mL 3-neck flask with a condenser and heated to 280 oC under N₂ flow. In a case of the Zn(OA)₂, 10 mmol of ZnO, 10 mL of OA, and 10 mL of 1-ODE were placed in 50 mL 3-neck flask with a condenser and heated to 300 °C under N₂ flow. In both cases, the color of the mixtures gradually changed from turbid brown (Cd solution) or cloudy (Zn solution) to optically-clear, which means that the cadmium oleate or zinc oleate has formed. At the end of reaction, the solutions were cooled down and kept at 50 oC for Cd(OA)₂ and 100 oC for Zn(OA)₂. In the meantime, for the TOPSe and TOPS, 1 mmol of elemental selenium was dissolved in 0.5 mL of TOP (TOPSe) and 8 mmol of elemental sulfur was dissolved in 4 mL of TOP (TOPS), in a N₂ atmosphere.

Red-emitting CdSe/CdS/CdZnS QDs were prepared by a one-pot multi-step procedure. For the CdSe core, 1 mmol of CdO, 3 mmol of My and 15 mL of 1-ODE were placed in 100 mL 3-neck flask and heated to 270 oC under N₂ flow. Once the mixture became optically clear, 0.25 mL of TOPSe was rapidly injected into the flask. After 3 min of reaction, 1.5 mmol of DDT and 2 mL of Zn(OA)₂ were added dropwise to the flask and the reaction temperature was increased to 300 °C. Over 30 min of reaction, the first CdS shell was overgrown on the core and Zn(OA)₂ monolayer was absorbed on the surface of CdS shell, which helps the subsequent growth of a CdZnS shell. At the end of reaction, 4 mL of Zn(OA)₂ and 1.5 mL of TOPS were added to the flask and 2 mL of Cd(OA)₂ was injected dropwise into the flask for 1 min. Throughout the following reaction for 9 min, a CdZnS shell was grown on previous CdSe/CdS QDs. Finally, an additional CdZnS shell was introduced by adding 6 mL of Zn(OA)₂, 2 mL of TOPS, and dropping 3 mL of Cd(OA)₂ for 1 min. After 5 min of reaction, the flask was quickly quenched to room temperature. The as-synthesized QDs were purified by precipitating with ethanol and re-dispersing in toluene repeatedly (5 times). The final products were dispersed in toluene and kept in the refrigerator.



Figure S 3. (a) A low magnification and (b) a high-resolution transmission electron microscopy images of red QDs (average diameter: 8.2 nm).

11. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized modifying the method reported by Pacholski et al.⁵ Firstly, 3 g of $Zn(ac)_2 \cdot 2H_2O$ and 120 mL of methanol were placed in 3-neck round bottom flask and heated to 60 °C. At that temperature, 60 mL KOH solution containing 1.51 g of KOH was added dropwise into the $Zn(ac)_2 \cdot 2H_2O$ solution with strong agitation. The reaction mixture was kept at 60 °C for 2 hr 15 min. At the end of reaction, the product appeared as a milky solution. After precipitating the product by centrifugation at 4000 rpm, the product was washed with methanol twice. Finally, the product was centrifuged again and redispersed in 5 mL of butanol.

12. UV-Visible and photoluminescence measurements



Figure S 4. (a) Absorption (dotted lines, left) and PL spectra (solid lines, right) of red QDs (red), BCP2 (blue), and BCP1 (green). (b) Photoluminescence spectra of pristine red QDs (solid line) and BCP2@redQD (dotted line).

This insignificant reduction of emission infers that the non-radiative energy transfer (i.e., Förster and Dexter energy transfer) or exciton dissociation (by type-II bandgap alignment) are inhibited. It is attributed to the thick inorganic shell of QDs. The thick shell provides a space between the QD cores and the conducting polymers, which prevents their electrical contact as well as reducing the energy transfer efficiency.

13. Thickness dependence of the E.Q.E.



Figure S 5. Maximum E.Q.E. with various thickness of hybrid light emitting layer.

From EQE-J curves, both devices have high efficiencies and well electron-hole balanced characteristics at around 40 and 45 nm thicknesses. In case of Device 1, it showed a drastic efficiency drop with increasing active layer thickness of more than 40 nm. This can be considered due to poor hole transporting properties between **BCP1** and red QDs since the high HOMO level of **BCP1** (-5.2 eV) creates an energetic barrier.

14. Notes:

a) We found that the ratio between the QDs and the polymer is very important for the efficiency of the LEDs. If the polymer content is too high, parasitic emission is observed, and if the content is too low, the film forming properties and charge transport become poor. We found the best results at a ratio of QDs to polymer of 3:1. For similar reasons, the concentration of the hybrid dispersion plays a big role. A concentration of 40 mg/mL was found to give the best results.

b) The device presented in Nano Letters⁶ was prepared with CBP (4,4'-Bis(N-carbazolyl)-1,1'-biphenyl) as hole injection layer, which has a HOMO level of about -6 to -6.3 eV.⁷ In this case, the hole injection barrier is lower than in the hybrid device, which was prepared with TPDF (HOMO level -5.9 eV). If we compare it with the device built with TCTA (HOMO level of -5.7 to -5.9 eV, also presented in Nano Letters), the efficiency is similar.

15. References:

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