# PCCP



# **Electronic Supplementary Information**

# Influence of $\pi$ -conjugation structural changes on intramolecular charge transfer and photoinduced electron transfer in donor- $\pi$ -acceptor dyads

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Synthetic details

## TABLE

Table S1. Steady-state absorption and emission parameters of dyads 1-3 in various solvents

|                   | dyad 1                |                      | dyad 2               |                     | dyad 3               |                     |
|-------------------|-----------------------|----------------------|----------------------|---------------------|----------------------|---------------------|
|                   | λ <sub>Abs</sub> (nm) | λ <sub>Em</sub> (nm) | $\lambda_{Abs}$ (nm) | $\lambda_{Em}$ (nm) | $\lambda_{Abs}$ (nm) | $\lambda_{Em}$ (nm) |
| n-hexane          | 292, 330              | 376                  | 292, 339             | 354                 | 292, 338             | 364                 |
| CHCl <sub>3</sub> | 294, 331              | 415                  | 294, 342             | 354, 415            | 294, 340             | 409                 |
| THF               | 293, 329              | 420                  | 293, 340             | 354, 429            | 293, 338             | 412                 |
| $CH_2CI_2$        | 294, 330              | 432                  | 293, 342             | 355, 446            | 293, 339             | 425                 |
| CH₃CN             | 292, 326              | 463                  | 292, 340             | 355, 508            | 292, 338             | 464                 |

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Fig. S1. Absorption spectra of dyads 1-3 in various solvents.



**Fig. S2.** (a) Dependence of concentration on emission spectra of dyad **2** (2.5–20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>.  $\lambda_{ex}$  = 270 nm. Inset shows the ratio of the emission intensities (I<sub>510 nm</sub>/I<sub>370 nm</sub>). (b) Dependence of concentration on the decay profiles of dyad **2** (1–8  $\mu$ M) monitored at different wavelength ranges: 350-400 and 450-550 nm for monomer and exciplex, respectively.

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**Fig. S3.** Contour images (a), transient absorption spectra (b) and decay profiles (c) of dyad **3** in  $CH_2Cl_2$ . The TA spectra were measured using different excitation wavelengths (column A; 290 nm, and column B; 340 nm) at long delay times (0-5000 ps) after 100 fs pulse excitation. The decay and rise profiles in (c) were monitored at selected wavelengths, respectively, as mentioned in figures.



**Fig. S4**. Contour images (a), transient absorption spectra (b) and decay profiles (c) of dyad **1** in CH<sub>2</sub>Cl<sub>2</sub>. The TA spectra were measured using different excitation wavelengths (column A; 290 nm, and column B; 340 nm) at long delay times (0-5000 ps) after 100 fs pulse excitation. The decay and rise profiles in (c) were monitored at selected wavelengths, respectively, as mentioned in figures.



Scheme S1. Energy and frontier orbital diagram for dyad 3 calculated by DFT with B3LYP function and 6-31G(d,p) basis using Gaussian 09 Program.<sup>S1</sup>

#### Synthetic details

#### 2-(4-((4-(9H-carbazol-9-yl)phenyl)dimethylsilyl) phenyl)-5phenyl-1,3,4-oxadiazole (dyad 1)

9-(4-bromophenyl)carbazole (PC-Br) (2.13 g, 6.6 mmol) in diethyl ether (40 mL) was stirred at 0°C under dry argon atmosphere and treated with a solution of *n*-BuLi (2.9 mL, 2.5 M in hexane, 7.3 mmol). The resulting mixture was kept at 0°C for 1 h, and then dichlorodimethylsilane (6.6 mL, 54.9 mmol) was added slowly. The reaction temperature was warm to room temperature and the reaction mixture was stirred for overnight. After the reaction, LiCl salts were filtered by reaction solvent and canuula and excess dichlorodimethlysilane in filtrate were removed under reduced pressure and stored in Ar atmosphere. In another flask, 2-(4bromophenyl)-5-phenyl-1,3,4-oxadiazole (DPOz-Br) (2.22 g, 7.4 mmol) in dry tetrahydrofuran (THF, 40 mL) was prepared and a 2.5 M solution of n-BuLi in n-hexane (2.9 mL, 7.3 mmol) was added dropwise at -78°C. After stirring for 30 min, the previously prepared 9-[4-(chlorodimethylsilyl)phenyl]-9Hcarbazole (PCz) in THF (10 mL) was added slowly at -78°C. After addition, the reaction temperature was warm to room temperature and the reaction mixture was stirred for overnight. The reaction mixture was quenched by addition of distilled water, extracted with dichloromethane and washed with water. The combined organic layers were dried over MgSO<sub>4</sub> and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using ethyl acetate/*n*-hexane (v/v = 1:4) as an eluent. The resulting white solid was dissolved in dichloromethane and evaporated slowly to give single crystals. Yield: 36%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.18–8.13 (m, 6H), 7.76 (t, J = 15.9 Hz, 4H), 7.6-7.53 (m, 5H), 7.48-7.38 (m, 4H), 7.31-7.26 (m, 2H), 1.58 (s, 3H), 0.70 (s, 3H); 13C NMR (75 MHz, CDCl3, δ): 142.9, 140.6, 138.8, 136.6, 135.7, 134.9, 131.8, 129.1, 126.9, 126.3, 126.1, 125.9, 124.5, 123.9, 123.4, 120.3, 120.0, 109.8, -2.46. HRMS: calculated for C<sub>34</sub>H<sub>27</sub>N<sub>3</sub>OSi: 521.1923, Found: 521.1931. Elemental analysis: calculated for

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C<sub>34</sub>H<sub>27</sub>N<sub>3</sub>OSi: C, 78.28; H, 5.22; N, 8.05, Found: C, 78.29; H, 5.23; N, 8.03.

#### 2-(4'-(9H-carbazol-9-yl)biphenyl-4-yl)-5-phenyl-1,3,4oxadiazole (dyad 2)

A mixture of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2'yl)phenyl)-9H-carbazole (PCz-BE) (1.49 g, 4.0 mmol), DPOz-Br (1.33 g, 4.4 mmol), tetrakis(triphenylphosphine)palladium (0.46 g, 0.4 mmol), and Na<sub>2</sub>CO<sub>3</sub> (1.71 g, 16.0 mmol) in THF/H<sub>2</sub>O (v:v = 21:7) was stirred at 70°C for overnight under argon atmosphere. After cooling to room temperature, the mixture was poured into distilled water and extracted with dichloromethane. The combined organic layers were dried over MgSO4 and evaporated under reduced pressure. The crude product was purified by recrystallization in dichloromethane/n-hexane to give a white solid. Yield: 76%; <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, δ): 8.29 (d, J = 8.5 Hz, 2H), 8.21-8.16 (m, 4H), 7.89 (t, J = 8.0 Hz, 5H), 7.71 (d, J = 8.5 Hz, 2H), 7.59-7.55 (m, 2H), 7.51-7.41 (m, 4H), 7.34-7.29 (m, 2H); 13C NMR (75.4 MHz, CDCl<sub>3</sub>, δ): 143.5, 140.7, 138.8, 137.8, 131.8, 129.1, 128.6, 127.7, 237.6, 127.5, 137.0, 126.0, 123.9, 123.5, 123.0, 120.4, 120.1, 109.78. HRMS: calculated for C<sub>32</sub>H<sub>21</sub>N<sub>3</sub>O: 463.1685, Found: 463.1689. Elemental analysis: calculated for C<sub>32</sub>H<sub>21</sub>N<sub>3</sub>O: C, 82.92; H, 4.57; N, 9.07, Found: C, 82.90; H, 4.58; N, 9.08.

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