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states in triazine-based donor-acceptor systems

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- 16

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Abstract: Six donor-acceptor systems with styrene based 9-phenyl carbazole, 19 4,4'-di(hydro, methyl, methoxy or octyloxy) triphenylamine and 4-methylphenyl 20 indoline derivatives as donors, and s-triazine group as the acceptor were synthesized 21 and characterized. The charge-separated states of these donor-acceptor systems were 22 generated through the effective photoinduced electron transfers from excited donor 23 modules to acceptor modules and had lifetimes ranging from 57 ns to 215 ns. These 24 donor-acceptor systems are capable of fast charge separation, but have extremely slow 25 charge recombination. The back electron transfer processes of these donor-acceptor 26 systems occur in the inverted region of the Marcus curve. The driving forces of back 27 28 electron transfer and the reorganization energies of electron transfer decrease in the order of 9-phenyl carbazole derivative, 4,4'-di(hydro, methyl, methoxy or octyloxy) 29 triphenylamine derivative and 4-methylphenyl indoline derivative. These two factors 30 work together to determine the different lifetimes of charge-separated states in these 31 donor-acceptor systems. 32

33

Keywords: Donor-acceptor system; Photoinduced electron transfer; Charge-separated
 state; Lifetime; Driving force; Reorganization energy

37 **1. Introduction**

In recent years, many researchers have expressed great interest in the simulation 38 39 of the long-lived charge-separated states of the reaction center in photosynthesis, where the cascade formation of short-range photoinduced energy transfer and 40 multistep electron transfer occurs [1-7]. A variety of supramolecular systems were 41 developed as a result of the integration of various donors and acceptors to obtain long 42 distance charge-separated states [8-15]. However, a large amount of energy is lost 43 during the multistep electron transfer processes to reach the final charge-separated 44 state in both natural and artificial photosynthetic reaction centers [16,17]. Additionally, 45 the difficulty of synthesizing these multistep electron transfer molecules has 46 prevented the practical applications for construction of energy conversion systems 47 48 [17].

Alternatively, attempts have been made to design simple and small 49 Donor-Acceptor (D-A) systems in such a way that charge separation occurs rapidly 50 51 and quantitatively, while charge recombination is somehow impeded [18]. According to the Marcus theory, the increase of the lifetime of charge-separated states was 52 accompanied with the decrease of the reorganization energy of electron transfer in the 53 Marcus inverted region. It is possible to obtain such simple D-A systems because the 54 reorganization energy of electron transfer is expected to reduce with decreasing D-A 55 distance [19]. Hence, a number of simple D-A systems were designed and synthesized 56 to obtain long-lived charge-separated states [18,20-24]. The relevant energy levels 57 determine the driving force of the electron transfer between the donor and acceptor 58

59 [25-30], while the distance, spatial orientation, and flexibility of molecules 50 significantly influence the rate of photoinduced electron transfer and the efficiency of 51 creating charge-separated states [25,31-35]. However, the design principle between 52 donor and acceptor, which aimed at increasing the lifetimes of charge-separated states 53 in simple D-A systems, is unclear and should be studied further.

Triphenylamine and indoline could act as an effective electron donor and 64 potentially be widely used in organic photovoltaic materials [36-41]. Triazine (TRC) 65 was confirmed as an effective electron-accepting module in D-A systems, which 66 67 could improve the electron-injection and electron-transportation abilities of its conjugated derivatives in previous studies by others [42-45] and our previous work 68 [46-49]. Therefore, we have designed and reported two D-A systems MTPA-TRC 69 70 [47-49] and YD-TRC [49], which used styrene based 4,4'-dimethyl-triphenylamine (MTPA) and 4-methylphenyl indoline (YD) as the donors, respectively, and triazine 71 group (TRC) as the acceptor. Two lifetimes of charge-separated states were obtained 72 such that MTPA⁺-TRC⁻ as 80 ns and YD⁺-TRC⁻ as 215 ns. The important conclusion 73 indicated was that YD module was more effective than MTPA in forming long-lived 74 charge-separated states, which should be discussed and explained systematically in 75 more detail. 76

Therefore, more compounds based on D-TRC system should be designed and characterized, and the relationship between the improvement of donor ability and the lifetime of charge-separated states of the D-TRC system should be clarified and defined in an intuitive way. To summarize the effect of tuning donors on lifetimes of

charge-separated states, we synthesized four new compounds of D-TRC systems, 81 which used the replacement and modification of triphenylamine moiety to achieve 82 83 different donor ability in comparison with MTPA-TRC. On one hand, styrene based non-substituted triphenylamine (TPA) and 9-phenyl carbazole (PCB) were alternatives 84 to MTPA and used to obtain TPA-TRC and PCB-TRC, respectively. On the other hand, 85 the dimethoxy groups and dioctyloxy groups were introduced to triphenylamine 86 moiety of TPA-TRC to construct the derivatives MeTPA-TRC and OeTPA-TRC, 87 respectively. Combining the results of these D-TRC systems with the reported results 88 of MTPA-TRC [48] and YD-TRC [49], this work will exhibit six D-TRC systems 89 which have the increased lifetimes of charge-separated states through the 90 enhancement of donor ability, and the reason for this conclusion will be discussed 91 92 systematically in this paper. Structures of key compounds characterized in this work are provided in Scheme 1, while MTPA-TRC and YD-TRC were synthesized and 93 studied previously. PCB-TRC, TPA-TRC, MeTPA-TRC and OeTPA-TRC were first 94 reported here and their synthetic routes were shown in Scheme 1. 95

96

97Scheme 1.....

98

99 Photophysical properties of these compounds were studied using both steady 100 state and transient UV-Vis and fluorescence measurements coupled with 101 electrochemical measurements and DFT calculations. The results of these 102 measurements and the corresponding analysis are provided in Section 3 following the

103	description	of	methods	in	Section	2.	Finally,	the	conclusions	of	this	work	are
104	summarized	lin	Section 4.										

- 105 **2. Experimental and computational methods**
- 106 2.1 Materials

3-(4-nitrostyryl)-9-phenyl-9H-carbazole (PCBn) [50], 4-(4-nitrostyryl)-triphen 107 ylamine (TPAn) [50], 4,4'-dimethyl-4"-(4-nitrostyryl)-triphenylamine (MTPAn) [5 108 0], 4,4'-dimethoxy-4"-(4-nitrostyryl)-triphenylamine (MeTPAn) [50], 4,4'-dioctylo 109 xy-4"-(4-nitrostyryl)-triphenylamine (OeTPAn) [50], 4-(4-methylphenyl)-7-(4-nitro 110 styryl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (YDn) [50], 4,4'-dimethyl-4"-(4 111 -(4,6-dichloro-1,3,5-triazin-2-ylamino)styryl) triphenylamine (MTPA-TRC) [48] an 112 d 4-(4-methylphenyl)-7-(4-(4,6-dichloro-1,3,5-triazin-2-ylamino)styryl)-1,2,3,3a,4,8b 113 -hexahydrocyclopenta[b]indole (YD-TRC) [49] were prepared according to the li 114 terature. The synthetic pathways of 3-(4-(4,6-dichloro-1,3,5-triazin-2-ylamino)styr 115 yl)-9-phenyl-9H-carbazole (PCB-TRC), 4"-(4-(4,6-dichloro-1,3,5-triazin-2-ylamino) 116 styryl)triphenylamine (TPA-TRC), 4,4'-dimethoxy-4"-(4-(4,6-dichloro-1,3,5-triazin-117 2-ylamino)styryl)-triphenylamine (MeTPA-TRC), 4,4'-dioctyloxy-4"-(4-(4,6-dichlor 118 o-1,3,5-triazin-2-ylamino)styryl)triphenylamine (OeTPA-TRC) were illustrated in 119 Scheme 1. All reagents and solvents were reagent grade and further purified b 120 y the standard methods when necessary. All synthetic procedures were carried 121 out under an atmosphere of dry nitrogen or dry argon unless otherwise indicate 122 123 d.

124 **TPAa.** TPAn (0.090 g, 0.23 mmol) was dissolved in absolute ethanol (40 mL) at

room temperature. Then $SnCl_2 \bullet 2H_2O$ (0.23 g, 1.0 mmol) was added into the solution.
Afterwards, the suspension was refluxed at 90 $^\circ$ C for 8 h. After filtration, the solid
was washed with absolute ethanol. Then the organic phases were condensed by rotary
evaporation. The product was further purified by column chromatography on silica
gel using cyclohexane: dichloromethane (3:2 v:v) as the eluent to yield a pale yellow
solid (0.060 g, 72%). HRMS-ESI: Found: $m/z=363.1855(M+H)^+$ (Calc. for $C_{26}H_{23}N_2^+$:
m/z=363.1856). ¹ H NMR (CDCl ₃ , 500 MHz), δ: 7.76-7.62 (m, 2H), 7.61-7.29 (m, 4H),
7.29-7.19 (m, 6H), 7.19-6.76 (m, 8H), 6.44 (s, 2H).
Synthetic procedures of MeTPAa, OeTPAa and PCBa are the same as that of
TPAa except that TPAn was replaced by MeTPAn (0.10 g, 0.23 mmol), OeTPAn (0.15
g, 0.23 mmol) and PCBn (0.090 g, 0.23 mmol), respectively. The characterization data

136 of these compounds are as follows. .

MeTPAa. A pale green solid (0.065 g, yield: 67%) was obtained by column
chromatography. HRMS-ESI: Found: m/z=423.2065 (M+H)⁺ (Calc. for C₂₈H₂₇N₂O₂⁺:
m/z=423.2067). ¹H NMR (CDCl₃, 500 MHz), δ: 7.48 (dd, J=26.1, 19.7 Hz, 1H), 7.37
(d, J=8.3 Hz, 1H), 7.33-7.25 (m, 5H), 7.17 (d, J=8.8 Hz, 1H), 7.04 (t, J=16.8 Hz, 3H),
6.94 (dd, J=16.4, 7.2 Hz, 1H), 6.86 (dd, J=32.0, 7.8 Hz, 6H), 5.31 (s, 2H), 3.79 (d,
J=9.1 Hz, 6H).

OeTPAa. A pale green solid (0.085 g, yield: 60%) was obtained by column
chromatography. HRMS-ESI: Found: m/z=619.4261 (M+H)⁺ (Calc. for C₄₂H₅₅N₂O₂⁺:
m/z=619.4258). ¹H NMR (CDCl₃, 500 MHz), δ: 7.86-7.69 (m, 2H), 7.67-7.33 (m, 6H),
7.33-7.21 (m, 2H), 7.21-6.77 (m, 6H), 6.20 (dd, J=8.1, 1.3 Hz, 2H), 4.32 (t, J=6.7 Hz,

147 2H), 4.06-3.83 (m, 4H), 2.11-0.56 (m, 30H).

148	PCBa. A yellow solid (0.060 g, yield: 73%) was obtained by column
149	chromatography. HRMS-ESI: Found: $m/z=361.1697$ (M+H) ⁺ (Calc. for $C_{26}H_{21}N_2^+$:
150	m/z=361.1699). ¹ H NMR (CDCl ₃ , 500 MHz), δ: 8.74-8.69 (m, 2H), 8.30 (s, 1H), 8.21
151	(dt, J=21.0, 10.5 Hz, 1H), 8.01 (dd, J=8.6, 1.4 Hz, 1H), 7.71-7.56 (m, 3H), 7.56-7.29
152	(m, 8H), 7.29-7.03 (m, 2H), 5.31 (s, 2H).

TPA-TRC. Cyanuric chloride (0.047 g, 0.26 mmol) was first dissolved in the 153 absolute tetrahydrofuran at 0 °C. Then TPAa (0.093 g, 0.26 mmol) was added into the 154 solution. Afterwards, the solution was warmed to and then kept stirring at room 155 temperature for 30 min. Then the solvent was removed by rotary evaporation and the 156 residue was purified by column chromatography on silica gel using petroleum ether : 157 dichloromethane (1:1 v:v) as the eluent to yield a yellow solid (0.11 g, 84%). 158 HRMS-ESI: Found: $m/z=510.1250 (M+H)^+$ (Calc. for $C_{29}H_{22}Cl_2N_5^+$: m/z=510.1247). 159 ¹H NMR (CDCl₃, 500MHz), δ: 7.62-7.43 (m, 5H), 7.39 (d, J=8.6 Hz, 2H), 7.27 (dd, 160 J=9.8, 5.9 Hz, 4H), 7.12 (d, J=7.8 Hz, 4H), 7.09-7.01(m, 5H), 6.97 (d, J=16.3 Hz, 1H). 161 ¹³C NMR (CDCl₃, 100.6 MHz), δ:171.42, 163.92, 147.59, 147.50, 136.42, 135.42, 162 134.57, 131.14, 129.31, 128.62, 127.05, 124.59, 123.45, 123.15, 121.36. Anal.: Found: 163 C, 68.09; H, 4.03; N, 13.51% (Calc. for C₂₉H₂₁Cl₂N₅: C, 68.24; H, 4.15; N, 13.72%). 164 Synthetic procedures of MeTPA-TRC, OeTPA-TRC and PCB-TRC are the same 165 as TPA-TRC except that TPAa was replaced by MeTPAa (0.11 g, 0.26 mmol), 166

167 OeTPAa (0.16 g, 0.26 mmol) and PCBa (0.094 g, 0.26 mmol), respectively. The

168 characterization data of these compounds are as follows.

169	MeTPA-TRC. A yellow solid (0.12 g, yield: 82%) was obtained by column
170	chromatography. HRMS-ESI: Found: $m/z=570.1460$ (M+H) ⁺ (Calc. for
171	$C_{31}H_{26}Cl_2N_5O_2^+$: m/z=570.1458). ¹ H NMR (CDCl ₃ , 500 MHz), δ : 7.57-7.46 (m, 2H),
172	7.33 (d, J=7.9 Hz, 2H), 7.46-7.08 (m, 4H), 7.08 (s, 1H), 7.06 (s, 2H), 7.10-6.90 (m,
173	3H), 6.84 (d, J=8.7 Hz, 5H), 3.81 (s, 6H). 13 C NMR (CDCl ₃ , 100.6 MHz), δ : 171.24,
174	163.91, 158.41, 147.46, 137.28, 135.47, 134.58, 131.43, 129.26, 128.62, 127.03,
175	126.95, 124.38, 121.33, 113.67, 55.50. Anal.: Found: C, 65.13; H, 4.28; N, 12.03%
176	(Calc. for C ₃₁ H ₂₅ Cl ₂ N ₅ O ₂ : C, 65.27; H, 4.42; N, 12.28%).
177	OeTPA-TRC. A yellow solid (0.16 g, yield: 78%) was obtained by column
178	chromatography. HRMS-ESI: Found: $m/z=766.3651$ (M+H) ⁺ (Calc. for
179	$C_{45}H_{54}Cl_2N_5O_2^+$: m/z=766.3649). ¹ H NMR (CDCl ₃ , 500 MHz), δ : 7.62-7.41 (m, 5H),
180	7.41-7.25 (m, 3H), 7.13-6.97 (m, 5H), 6.97-6.72 (m, 6H), 3.95 (dt, J=13.0, 6.5 Hz,
181	4H), 1.96-1.61 (m, 4H), 1.55-1.38 (m, 4H), 1.38-1.24 (m, 11H), 1.38-1.02 (m, 11H).
182	¹³ C NMR (CDCl ₃ , 100.6 MHz), δ: 171.26, 163.68, 158.63, 147.55, 136.26, 135.49,
183	134.56, 131.93, 129.09, 128.73, 127.25, 126.83, 126.72, 124.71, 121.42, 120.22,
184	115.32, 68.32, 31.95, 31.86, 29.73, 29.41, 29.28, 26.12, 22.69, 14.14. Anal.: Found: C,
185	70.32; H, 6.85; N, 8.97% (Calc. for C ₄₅ H ₅₃ Cl ₂ N ₅ O ₂ : C, 70.48; H, 6.97; N, 9.13%).
186	PCB-TRC. A pale green solid (0.11 g, yield: 80%) was obtained by column
187	chromatography. HRMS-ESI: Found: $m/z=508.1091 (M+H)^+$ (Calc. for $C_{29}H_{20}Cl_2N_5^+$:
188	m/z=508.1090). ¹ H NMR (CDCl ₃ , 500 MHz), δ: 8.28 (s, 1H), 8.18 (d, J=7.8 Hz, 1H),
189	7.68-7.37 (m, 10H), 7.35-7.24 (m, 5H), 7.15 (d, J=16.2 Hz, 1H), 5.30 (s, 1H). ¹³ C

190 NMR (CDCl₃, 100.6 MHz), δ : 171.40, 163.89, 141.38, 137.53, 137.02, 136.34,

- 191 135.65, 132.42, 129.93, 129.40, 128.64, 127.60, 127.05, 126.99, 126.22, 123.82,
- 192 123.33, 122.34, 121.37, 121.18, 120.37, 118.62, 110.06. Anal.: Found: C, 68.43; H,

193 3.62; N, 13.59% (Calc. for $C_{29}H_{19}Cl_2N_5$: C, 68.51; H, 3.77; N, 13.78%).

- 194 **2.2 Mass spectrometry**. The ESI mass spectra were obtained on a Thermo Fisher
- 195 LCQ Deca XP MAX mass spectrometer. MALDI-TOF mass spectra were obtained on
- a Bruker Autoflex tof/tofIII mass spectrometer.
- 197 **2.3 NMR spectrometry**. ¹H NMR spectra and ¹³C NMR spectra were obtained on a
- 198 VARIAN INOVA 500MHz spectrometer, and the testing temperature was set to 25 °C.
- 199 **2.4 Elemental analysis.** Elemental analysis for carbon, hydrogen, and nitrogen was
- 200 determined on a VARIO EL CUBE (ELEMENTAR, Germany) elemental analyzer.
- 201 **2.5 Thermogravimetric analysis (TGA).** Thermogravimetric analysis was performed
- 202 on a Rigaku Thermo plus TG 8120 instrument. The thermal stability of the samples
- was determined by measuring the weight loss while heating at a rate of 10 $^{\circ}$ C min⁻¹

from room temperature to 500 °C under the nitrogen atmosphere.

- 205 2.6 Differential scanning calorimetry (DSC). Differential scanning calorimetry at a
 206 heating rate of 10 °C min⁻¹ from 50 to 250 °C was performed using a TA DSC Q 20
 207 instrument under the nitrogen atmosphere.
- 208 **2.7 Cyclic voltammetry.** The electrochemical properties were measured using a BAS 209 100W electrochemical analyzer utilizing the three-electrode configuration with a 210 glassy carbon electrode as the working electrode, Ag/AgNO₃ electrode as the 211 reference electrode, and platinum as the auxiliary electrode. The analyzer was 212 calibrated using a ferrocene/ferrocenium redox couple as the external standard prior to

the measurements. The scan rate was set to 30 mV/s. Dichloromethane containing 0.1 mol•L⁻¹ tetra-butylammonium hexafluorophosphate (TBAPF₆) was employed as the medium for the cyclic voltammetric determination. The compound concentration was 5×10^{-4} mol•L⁻¹.

2.8 Computational details. Geometry optimizations of the molecules were carried 217 out using the three-parameter exchange functional of Becke and correlation functional 218 of Lee, Yang, and Parr (B3LYP) [51-53] with the 6-31G(d, p) basis set in toluene 219 without any symmetry constraints. The polarized continuum model (PCM) framework 220 [54] was used to describe the solvent effect. The SCF convergence was 10^{-8} a.u. the 221 gradient and energy convergence was 10^{-4} a.u. and 10^{-5} a.u., respectively. All 222 calculations were performed using the Gaussian09 package [55]. In order to confirm 223 the optimized geometry as a global minimum, frequency calculations at the same level 224 of theory were performed. A detailed description of computational methods can also 225 be found in our previous work [48]. 226

227 2.9 UV-Vis spectroscopy in solution. The absorption spectra were taken on a Thermo
228 Spectronic, Helios Gamma spectrometer. Quartz cells with a path length of 1 cm were
229 used to observe absorption in the UV region.

230 2.10 Fluorescence spectroscopy in solution. The fluorescence spectra were recorded
231 on a Varian CARY ECLIPSE fluorospectrophotometer.

232 2.11 Time-correlated single photon counting (TC-SPC). Excitation of samples was
233 done with picosecond diode lasers (Horiba JobinYvon Instruments) at 366 nm, and the
234 time resolution was ~ 150 ps. The laser pulse energy was ca. 15 pJ and attenuated

(often more than an order of magnitude) to the desired count rate of ca. 1% or less of 235 the excitation frequency. A cooled (ca. -40 °C) Hamamatsu MCP- photomultiplier 236 R3809U 51 was used for detection of single photons, and the signal passed through a 237 discriminator (Ortec 9307) and into a TAC (Ortec 566, 100 ns range used). The 238 electrical trigger signal from the laser was also passed through a discriminator 239 (Tennelec TC454) and onto the TAC (Ortec 566). The TAC output was read by a 240 DAQ-1 MCA computer card using 1024 channels and collected with 241 HoribaJobinYvon Data Station 2.5. Measurements were made in reverse mode at 5 242 MHz and under magic angle polarization. A cutoff filter, GG400 (Excitation at 366 243 nm), was used to block stray excitation light. A dilute solution of Ludox was used to 244 record the instrument response function without any filter for solution measurements. 245 No monochromator was used; i.e., all wavelengths transmitted by the cut off filter 246 were collected. The sample concentrations were 5×10^{-6} mol·L⁻¹, and the solutions 247 were bubbled with argon for 30 min before the measurements. 248

2.12 Nanosecond transient absorption spectroscopy. Nanosecond transient 249 absorption measurements were performed on a LP-920 laser flash photolysis setup 250 (Edinburgh). Excitation at 420 nm with a power of 2.0 mJ per pulse from a 251 computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant 355 II) 252 operating at 10 Hz was directed to the sample. The laser and analyzing light beams 253 passed perpendicularly through a 1 cm quartz cell. The complete time-resolved 254 spectra were obtained using a gated CCD camera (AndoriSTAR); the kinetic traces 255 were detected by a Tektronix TDS 3012B oscilloscope and a R928P photomultiplier 256

and analyzed by Edinburgh analytical software (LP920). The samples used in the flash photolysis experiments were bubbled with argon for 30 min before measurements. The compound concentrations were 5×10^{-5} mol·L⁻¹.

260 **3. Results and discussion**

We characterized and compared PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC for the studies of photophysical processes. We performed electrochemical and spectroscopic measurements and computational calculations on these compounds. The results from these studies are discussed as follows.

266 **3.1 Thermal properties**

The thermal properties of the six compounds were investigated by thermal 267 gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under the 268 nitrogen atmosphere (Figure 1). TGA curves (Figure 1a) revealed the onset 269 temperatures (Td) of PCB-TRC, TPA-TRC, MTPA-TRC, decomposition 270 MeTPA-TRC, OeTPA-TRC and YD-TRC were 294 °C, 283 °C, 281 °C, 236 °C, 271 222 °C, 249 °C, respectively, indicating that these six compounds had the relatively 272 high thermal-stability. Additionally, the glass transition temperatures (Tg) of six 273 compounds were obtained in the range of 96-99 °C by analyzing the DSC 274 thermograms (Figure 1b). The values of Td and Tg of YD-TRC are smaller than those 275 of PCB-TRC and TPA-TRC, and the introduction of octyloxy groups obviously 276 reduces the values of Td and Tg of OeTPA-TRC in comparison with those of 277 TPA-TRC. 278

279	
280	Figure 1
281	
282	3.2 Electrochemical & Computational results
283	To reveal the orbital energy levels of these six compounds, the electrochemical
284	behaviors were investigated by cyclic voltammetry. The electrochemical
285	measurements are shown in Figure 2. The oxidation and reduction potentials as well
286	as the frontier orbital energies derived from these measurements are summarized in
287	Table 1.
288	
289	
290	Table 1
291	
292	As shown in Figure 2, PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC,
293	OeTPA-TRC and YD-TRC present the reversible oxidation waves, which could be
294	attributed to PCB, TPA, MTPA, MeTPA, OeTPA and YD modules, respectively, and
295	the irreversible reduction wave ascribed to the TRC module [48]. As shown in Table 1,
296	the charge transition first occurs in donor module from the highest occupied
297	molecular orbital (HOMO) to the lowest unoccupied molecular orbital plus one
298	(LUMO+1), and then the electron transfer from LUMO+1 to LUMO is possible in
299	these D-TRC systems. It can be concluded that all six molecules are typical D-A
300	systems with PCB, TPA, MTPA, MeTPA, OeTPA and YD as electron donors and the

301	TRC module as electron acceptor. Meanwhile, the computational results (Figure 3)
302	show that the HOMO and LUMO+1 are located at the donor modules and TRC
303	module respectively. It should be noted that the LUMO and LUMO+1 energy levels
304	of these studied D-A systems are within the error bar and can have the same energy.
305	
306	Figure 3
307	
308	As shown in Table 1, even though there is little difference of LUMO level among
309	these compounds, the HOMO level of PCB-TRC is lower than that of TPA-TRC by
310	0.15 eV. The HOMO levels of MTPA-TRC, MeTPA-TRC and OeTPA-TRC
311	introduced by methyl groups, methoxy groups and octoxy groups increased by 0.03
312	eV, 0.19 eV and 0.24 eV, respectively. In comparison with the triphenylamine
313	derivatives, YD-TRC has the highest HOMO level in these D-A systems. This
314	demonstrates that donor modules with stronger electron donating abilities (PCB $<$
315	TPA < MTPA < MeTPA < OeTPA < YD) have the stronger promoted effects on the
316	HOMO levels, but have little effects on LUMO levels in the D-A systems.
317	3.3 Absorption and fluorescence properties
318	The UV-vis absorption spectra of PCB-TRC, TPA-TRC, MTPA-TRC,
319	MeTPA-TRC, OeTPA-TRC and YD-TRC in toluene are shown in Figure 4. All six
320	compounds show two obvious absorption bands from 200 nm to 600 nm in toluene.

321 The bands appeared at 300 nm are due to the π - π * transition of 9-phenyl carbazole,

322 triphenylamine and 4-methylphenyl indoline. The maximum absorption bands are

323	ascribed to the intramolecular charge transfer (ICT) transitions. Once the methyl
324	groups, methoxy groups and octoxy groups are introduced to triphenylamine, the
325	absorption maxima of MTPA-TRC, MeTPA-TRC and OeTPA-TRC become 393 nm,
326	396 nm and 397 nm, which are red-shifted 7nm, 10nm and 11nm from 386 nm of
327	TPA-TRC, respectively. Both PCB-TRC and YD-TRC have lower absorption
328	intensities than TPA-TRC. The absorption maxima of PCB-TRC and YD-TRC are at
329	359 nm and 402 nm, which are blue-shifted 27 nm and red-shifted 16 nm, respectively,
330	in comparison with that of TPA-TRC. The absorption maxima of these D-A systems
331	in order of decreasing wavelength is YD-TRC > OeTPA-TRC > MeTPA-TRC >
332	MTPA-TRC > TPA-TRC > PCB-TRC which is in agreement with the degree of
333	enhanced ICT character of donor modules in the D-A systems (YD $>$ OeTPA $>$
334	MeTPA > MTPA > TPA > PCB).
335	
336	Figure 4
337	
338	To explore the differences of photophysical processes from the excited donor
339	(PCB, TPA, MTPA, MeTPA, OeTPA and YD) module to acceptor (TRC) module, the

(PCB, TPA, MTPA, MeTPA, OeTPA and YD) module to acceptor (TRC) module, the
fluorescence spectra at the excitation wavelength of 380 nm were exhibited in toluene
(Figure 5). The emission maxima are in a series of decreasing wavelength of
OeTPA-TRC (470 nm), MeTPA-TRC (468 nm), MTPA-TRC (444 nm), TPA-TRC
(437 nm) and PCB-TRC (424 nm). However, the emission maxima of YD-TRC (452
nm) is significantly blue-shifted compared with that of OeTPA-TRC, which

345	corresponds to a much smaller Stokes shift of YD-TRC. It implies that the structure
346	reorganization of YD-TRC upon photoexcitation is the smallest among these D-A
347	systems.
348	
349	Figure 5
350	
351	Meanwhile, the fluorescence quantum yields (Φ) were obtained as 0.005, 0.054,
352	0.055, 0.108, 0.132 and 0.018 for PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC,
353	OeTPA-TRC and YD-TRC molecules, respectively. Taking reported compound
354	MTPA-TRC for instance, its fluorescence intensity is substantially quenched in
355	comparison with that of the compound MTPA [56] (Φ =0.690). The fluorescence of
356	MTPA-TRC follows a bi-exponential decay equation from the emission fluorescence
357	decay experiments: the fast component (0.29 ns) of the fluorescence is assigned to the
358	electron transfer from MTPA to the TRC module, which results in a charge-separated
359	state of MTPA ^{.+} -TRC , and the slow component (1.73 ns), which is attributed to the
360	solvation relaxation of MTPA singlet. We also carried out the emission fluorescence
361	decay experiments to investigate the fluorescence of the other five compounds (Figure
362	6). It is clear that the fluorescence from PCB, TPA, MeTPA, OeTPA and YD modules
363	follow the bi-exponential decay process. The emission lifetimes and proportions are
364	provided in Table 2, illustrating that the photoinduced electron transfer, which is
365	attributed to the short lifetime should lead to the low fluorescence yield of these D-A
366	systems.
367	

369**Table 2**.....

370

Interestingly, different donor modules affect the emission lifetimes and 371 proportions of the fluorescence decay of D-A systems differently. As shown in Table 372 2, the lifetimes of fluorescence for PCB-TRC and YD-TRC are obviously larger than 373 those of TPA-TRC, MTPA-TRC, MeTPA-TRC and OeTPA-TRC. The proportions of 374 the fluorescence decay related to photoinduced electron transfer are different in these 375 376 six compounds. The proportion of photoinduced electron transfer is given in decreasing value in these D-A systems (66.8% for YD-TRC > 64.3% for 377 OeTPA-TRC > 45.9% for MeTPA-TRC > 39.7% for MTPA-TRC > 33.9% for 378 TPA-TRC > 12.3% for PCB-TRC). This result reveals that using the YD module as 379 the donor in these D-A systems should be more effective than other donor modules to 380 form the long-lived charge-separated states. 381

Therefore, to determine the lifetimes of charge-separated states for compounds 382 PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC, and YD-TRC, 383 nanosecond transient absorption measurements have been performed. As we reported 384 previously, there is no signal for the triplet absorption by compounds MTPA and YD, 385 and the positive transient absorptions of MTPA-TRC and YD-TRC in the range 386 400-700 nm were attributed to the MTPA⁺ and YD⁺ absorptions [48,49]. The 387 absorptions of PCB^{.+}, TPA^{.+}, MeTPA^{.+} and OeTPA^{.+} should be similar with that of 388 MTPA⁺. The lifetimes of charge-separated states of MTPA⁺-TRC⁻ and YD⁺-TRC⁻ 389 390 were reported as 80ns [48] and 215 ns [49], respectively. Meanwhile, the lifetimes of charge-separated states PCB⁺-TRC⁻, TPA⁺-TRC⁻, MeTPA⁺-TRC⁻, OeTPA⁺-TRC⁻ 391 were estimated as 57 ns, 75 ns, 115 ns and 131 ns, respectively, and have been 392 393 exhibited in Figure 7 (a)-(d). It is obvious that the lifetimes of six compounds are in

394	the increasing order shown as PCB-TRC < TPA-TRC < MTPA-TRC < MeTPA-TRC
395	< OeTPA-TRC < YD-TRC, which is also in agreement with the degree of enhanced
396	ICT character of donor modules in the D-A systems (PCB < TPA < MTPA < MeTPA
397	< OeTPA < YD).
398	
399	Figure 7
400	
401	3.4 Decay pathways of charge-separated states in PCB-TRC, TPA-TRC,
402	MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC
403	Here we derive and compare the decay pathways and charge-separated states
404	lifetimes of PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC and
405	YD-TRC. It is beneficial to comprehend the principle of tuning the donors to control
406	the lifetimes of charge-separated states in these triazine-based D-A systems. It also
407	exhibits the photoinduced electron transfer from LUMO of donor modules (LUMO+1)
408	to the LUMO of TRC module, which then generates the respective charge-separated
409	states. The energy diagram and photophysical processes of six compounds were
410	therefore constructed and exhibited in Figure 8.
411	
412	
413	
414	In PCB-TRC, about 12.3% of excited singlet PCB decay to the photoinduced
415	electron transfer pathway to form the charge-separated state, which is less than that of
416	TPA-TRC as about 33.9%. For MTPA-TRC, MeTPA-TRC, OeTPA-TRC and

YD-TRC about 39.7%, 45.9%, 64.3% and 66.8% of donor singlet excited states
convert into the charge-separated states through the photoinduced electron transfer
pathway, respectively. The value in YD-TRC is significantly larger than those in other
D-A systems. This demonstrates that the tuning of the donors to control photoinduced
electron transfer was reasonable and effective, which will change the quantum yield
of long-lived charge-separated states in D-A systems.

The Marcus theory of electron transfer offers a valuable guide to controlling and optimizing the efficiency of charge separation versus charge recombination. According to the Marcus theory of electron transfer [57], the rate constants of both forward electron transfer and back electron transfer are given by eq (1), where *V* is the electronic coupling matrix element, K_B is the Boltzman constant, *h* is the Planck constant, and *T* is the absolute temperature, ΔG_{ET} is the free energy change of electron transfer, and λ is the reorganization energy of electron transfer.

430
$$k_{ET} = \left(\frac{4\pi^3}{h^2\lambda k_BT}\right)^{1/2} V^2 ex \, p \left[-\frac{(\Delta G_{ET} + \lambda)^2}{4\lambda k_BT}\right] \tag{1}$$

431 ΔG_{ET} is the free energy change of electron transfer, and λ is the reorganization 432 energy of electron transfer.

The most significant concept of the Marcus theory is that the electron transfer rate constant is expected to decrease as the driving force of electron transfer ($-\Delta G_{ET}$) increases in the region where the driving force is larger than the reorganization energy of electron transfer ($-\Delta G_{ET} > \lambda$) [17]. This region ($-\Delta G_{ET} > \lambda$) is referred to as the Marcus inverted region [58-61]. The reorganization energy of electron transfer (λ) is the energy required to structurally reorganize the donor, acceptor and their solvation

spheres upon electron transfer [17]. λ is one of the most important terms, which has a strong impact on the lifetime and quantum yield. The small reorganization energy of electron transfer reactions and large driving force of back electron transfer are required to form long-lived charge-separated states [62-65].

The driving force $(-\Delta G_{BET} \text{ in eV})$ for back electron transfer process from TRC radical anion to donor radical cation were calculated by eq (2), where *e* stands for the elementary charge, $E_{OX}^0(D^{+}/D)$ is the first one-electron oxidation potential of the donor module, while $E_{RED}^0(A^{-}/A)$ refers to the first one-electron reduction potential of the acceptor moiety [57].

$$-\Delta G_{BET} = e \left[E_{OX}^{0} (D^{+}/D) - E_{RED}^{0} (A^{-}/A) \right]$$
(2)

Furthermore, the forward electron transfer driving force $(-\Delta G_{ET} \text{ in eV})$ is determined by eq (3), $\Delta E_{0.0}$ is the energy of the 0-0 transition energy gap between the lowest excited state and the ground state [57]. The driving forces of forward electron transfer ($-\Delta G_{ET}$) and back electron transfer ($-\Delta G_{BET}$), the rate constants of forward electron transfer (k_{ET}) and back electron transfer (k_{BET}) were calculated and shown in Table 3.

$$-\Delta G_{ET} = \Delta E_{0.0} + \Delta G_{BET} \tag{3}$$

From Table 3 we can see photoinduced forward electron transfer processes in these D-A systems are extremely rapid, and back electron transfer processes are up to three orders of magnitude slower. We investigated the electron transfer processes of these D-A systems at a specific temperature (298 K) and also estimated the values of λ and V according to eq (1) (Table 3) and drew the driving forces dependence of

461	intramolecular electron transfer rate constants of these D-A systems (Figure 9).
462	
463	
464	Figure 9
465	
466	It elucidates that back electron transfer processes in these D-TRC systems occur
467	in the inverted region of the Marcus curve, which plays a key role in the differences of
468	charge-separated state lifetimes for these D-A systems. The forward electron transfer
469	processes of PCB-TRC, TPA-TRC, MTPA-TRC are situated in the normal region of
470	the Marcus curve, and the forward electron transfer processes of MeTPA-TRC and
471	OeTPA-TRC are located in the beginning of the inverted region. For YD-TRC, the
472	forward electron transfer process is within the deeply inverted region of the Marcus
473	curve. As illustrated in table 3 and Figure 9, the driving forces of the back electron
474	transfer decrease gradually in the order of PCB-TRC > TPA-TRC > MTPA-TRC >
475	MeTPA-TRC > OeTPA-TRC > YD-TRC. The reorganization energies also decrease
476	in the same order, and are used to determine the rate constants of back electron
477	transfer in these D-A systems. These two factors work together to determine the
478	differences of lifetimes of charge-separated states of PCB-TRC < TPA-TRC <
479	MTPA-TRC < MeTPA-TRC < OeTPA-TRC < YD-TRC. It should be noted that the
480	electronic coupling matrix element of YD-TRC is clearly larger than that of other D-A
481	systems, which demonstrates that the electronic coupling of electron transfer
482	processes of YD-TRC is enhanced remarkably.

Above all, there are two reasons that account for differences in the lifetimes of the charge-separated states among these D-TRC systems: one is the driving force of back electron transfer and the other is the reorganization energy of electron transfer. These two factors work together to determine the different lifetimes of charge-separated states in these D-A systems.

488 **4.** Conclusions

In this paper, we designed and synthesized four new D-A systems PCB-TRC, 489 TPA-TRC, MeTPA-TRC, OeTPA-TRC, together with some results of two reported 490 D-TRC systems, MTPA-TRC and YD-TRC, to compare their photophysical processes 491 using steady-state and transient absorption and fluorescence spectra as well as the 492 electrochemical measurements and computational calculations. Meanwhile, the 493 thermal properties of six compounds had been studied by TGA and DSC. In the above 494 D-TRC systems, charge-separated states, PCB⁺-TRC⁻, TPA⁺-TRC⁻, MTPA⁺-TRC⁻, 495 MeTPA⁺-TRC⁻, OeTPA⁺-TRC⁻ and YD⁺-TRC⁻, were generated through the effective 496 photoinduced electron transfer with the lifetimes of 57 ns, 75 ns, 80 ns, 115 ns, 131 ns 497 and 215 ns, respectively. 498

In accordance with the Marcus theory of electron transfer, these simple D-TRC systems are capable of fast charge separation, but have extremely slow charge recombination, and the back electron transfer processes of these D-TRC systems occur in the inverted region of the Marcus curve. The back electron transfer driving forces decrease in the order of PCB-TRC > TPA-TRC > MTPA-TRC > MeTPA-TRC > OeTPA-TRC > YD-TRC. The reorganization energies decrease in the same order as

505	the back electron transfer driving forces, and are used to determine the rate constants
506	of back electron transfer in these D-A systems. The electron transfer driving forces
507	and reorganization energies of electron transfer work together to determine the
508	different lifetimes of charge-separated states in these simple D-TRC systems.
509	This work indicates that tuning donor ability to control the lifetime of
510	charge-separated state in D-A system was reasonable and achievable while providing
511	an important theoretical basis for the design of organic optoelectronic materials.
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720 Figures and Table captions:

- 721 Scheme 1 Synthesis scheme of key compounds
- Figure 1 TGA (a) and DSC (b) curves of PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red),

723 MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange).

- 724 Figure 2 Electrochemical curves of PCB-TRC (a), TPA-TRC (b), MTPA-TRC (c), MeTPA-TRC
- 725 (d), OeTPA-TRC (e) and YD-TRC (f) in dichloromethane vs Ag/Ag+. The concentration is

726 5×10^{-4} mol·L⁻¹. The data of MTPA-TRC and YD-TRC were taken from Ref. 48 and Ref. 49,

- respectively, for comparison purposes.
- 728 Figure 3 Some molecular orbitals and the corresponding energies of PCB-TRC, TPA-TRC,
- MTPA-TRC, MeTPA-TRC and YD-TRC obtained using B3LYP/6-31G(d, p) in toluene. The blue,
 grey, green, and white spheres represent nitrogen, carbon, chloride, and hydrogen atoms,
 respectively.
- Figure 4 Absorption spectra of PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red),
 MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange) in toluene. (Concentration:
- 734 $5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$).
- **Figure 5** Normalized fluorescence emission spectra excited at 380 nm of PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red), MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange) in toluene. (Concentration: 5×10^{-6} mol•L⁻¹).
- **Figure 6** Fluorescence emission decay spectra of PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red), MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange) in toluene. The excitation wavelength is 366 nm and the emission wavelength is 440 nm. The concentration is 5×10^{-6} mol•L⁻¹.
- **Figure 7** Transient absorption kinetics at 600 nm of PCB-TRC (a), TPA-TRC (b), MeTPA-TRC (c), OeTPA-TRC (d) in toluene following excitation with 410 nm, 8 ns laser pulses (Concentration: 5×10^{-5} mol·L⁻¹). The cyan lines are the fitting curves by the single-order exponential decay equation.
- Figure 8 Energy-level diagram and photophysical processes of PCB-TRC, TPA-TRC,
 MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC. The data of MTPA-TRC and YD-TRC
 were taken from Ref. 48 and Ref. 49, respectively, for comparison purposes.
- **Figure 9** Driving force $(-\Delta G_{ET} \text{ and } -\Delta G_{BET})$ dependence of intramolecular electron transfer rate constants in PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red), MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange). (Forward electron transfer: triangles; back electron transfer: circles).

Table 1 Electrochemical data obtained vs Ag/Ag⁺ in dichloromethane and frontier orbital energies

- **Table 2** Fluorescence quantum yields (Φ_f), emission lifetimes (τ_f) and fractions (in parentheses) of
- PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC in toluene bysteady and fitting transient spectra with exponential decay equations.
- **Table 3** The driving forces of forward electron transfer $(-\Delta G_{ET})$ and back electron transfer ($-\Delta G_{BET}$), respective rate constants (k_{ET} and k_{BET}), reorganization energies (λ) and electron coupling matrix element (V) in PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC.





Figure 1. TGA (a) and DSC (b) curves of PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red),
MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange).



(d), OeTPA-TRC (e) and YD-TRC (f) in dichloromethane vs Ag/Ag^+ . The concentration is 5×10^{-4} mol•L⁻¹. The data of MTPA-TRC and YD-TRC were taken from Ref. 48 and Ref. 49, respectively, for comparison purposes.



Figure 3. Some molecular orbitals and the corresponding energies of PCB-TRC, TPA-TRC,
MTPA-TRC, MeTPA-TRC and YD-TRC obtained using B3LYP/6-31G(d, p) in toluene. The blue,
grey, green, and white spheres represent nitrogen, carbon, chloride, and hydrogen atoms,
respectively.



Figure 4. Absorption spectra of PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red),
MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange) in toluene. (Concentration: 5×10⁻⁶ mol•L⁻¹).



Figure 5. Normalized fluorescence emission spectra excited at 380 nm of PCB-TRC (olive),
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Figure 7. Transient absorption kinetics at 600 nm of PCB-TRC (a),TPA-TRC (b), MeTPA-TRC (c), OeTPA-TRC (d) in toluene following excitation with 410 nm, 8 ns laser pulses (Concentration: 5×10^{-5} mol·L⁻¹). The cyan lines are the fitting curves by the single-order exponential decay equation.



914 Figure 8. Energy-level diagram and photophysical processes of PCB-TRC, TPA-TRC,
915 MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC. The data of MTPA-TRC and YD-TRC
916 were taken from Ref. 48 and Ref. 49, respectively, for comparison purposes.
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Figure 9. Driving force $(-\Delta G_{ET} \text{ and } -\Delta G_{BET})$ dependence of intramolecular electron transfer rate constants in PCB-TRC (olive), TPA-TRC (black), MTPA-TRC (red), MeTPA-TRC (blue), OeTPA-TRC (magenta) and YD-TRC (orange). (Forward electron transfer: triangles; back electron transfer: circles).

Compound	$E_{1/2}^{+/0, b)}$	$E_{1/2}^{0/-, b)}$	$E_{HOMO}^{c)}$	$E_{LUMO}^{c)}$	$E_g(opt)$	$E_{LUMO+1}^{d)}$
Compound	(V)	(V)	(eV)	(eV)	(eV)	(eV)
PCB-TRC	0.73	-1.21	-5.66	-3.72	2.95	-2.71
TPA-TRC	0.58	-1.21	-5.51	-3.72	2.82	-2.69
MTPA-TRC ^{a)}	0.55	-1.19	-5.48	-3.74	2.78	-2.70
MeTPA-TRC	0.39	-1.20	-5.32	-3.73	2.73	-2.59
OeTPA-TRC	0.34	-1.22	-5.27	-3.71	2.68	-2.59
YD-TRC ^{a)}	0.28	-1.19	-5.21	-3.74	2.56	-2.65

933 Tab	e 1. Electrochem	ical data obtai	ned vs Ag/Ag ⁺	in dichlorometl	hane and frontie	r orbital energi	es
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a) The data of MTPA-TRC and YD-TRC were taken from Ref. 48 and Ref. 49, respectively, f or 934

935 comparison purposes;

b) V vs Ag/Ag⁺, the potential of Ag/Ag⁺ was measured as 0.19 V vs SCE; 936

c) $E_{HOMO} = -E_{1/2}^{+/0} - 4.93 \text{ eV}, E_{LUMO} = -E_{1/2}^{-0/2} - 4.93 \text{eV};$ 937

d) $E_{LUMO+I} = E_{HOMO} + E_g(opt)$, the $E_g(opt)$ (optical band gap) was estimated from the onset of the 938

- of re ICT absorption band of respective compounds. 939
- 940

Table 2. Fluorescence quantum yields (Φ_j) , emission lifetimes (τ_f) and fractions (in parentheses) 942 of PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC and YD-TRC in toluene by 943 steady and fitting transient spectra with exponential decay equations.

	Ŧ	Emission lifetime, τ_f / ns (fraction %)
Compound	$arPsi_f$	λ_{ex} =366 nm, λ_{em} =440 nm
PCB-TRC	0.005	0.83 (12.3) 4.02 (87.7)
TPA-TRC	0.054	0.35 (33.9) 1.45 (66.1)
MTPA-TRC	0.055	0.29 (39.7) 1.73 (60.3)
MeTPA-TRC	0.108	0.20 (45.9) 2.04 (54.1)
OeTPA-TRC	0.132	0.25 (64.3) 2.12 (35.7)
YD-TRC	0.018	0.82 (66.8) 4.62 (33.2)

Table 3. The driving forces of forward electron transfer $(-\Delta G_{ET})$ and back electron transfer 948 $(-\Delta G_{BET})$, respective rate constants (k_{ET} and k_{BET}), reorganization energies (λ) and electron coupling 949 matrix element (V) in PCB-TRC, TPA-TRC, MTPA-TRC, MeTPA-TRC, OeTPA-TRC and 950 YD-TRC.

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	$-\Delta G_{ET}$	$-\Delta G_{BET}$	k_{ET}	k _{BET}	λ	V
Compound	(eV)	(eV)	$(\times 10^9 \text{s}^{-1})$	$(\times 10^{6} {\rm s}^{-1})$	(eV)	(cm ⁻¹)
PCB-TRC	0.99	1.94	1.20	17.54	1.19	2.67
TPA-TRC	1.05	1.79	2.86	13.33	1.03	3.38
MTPA-TRC	1.05	1.74	3.45	12.50	0.98	3.75
MeTPA-TRC	1.06	1.59	5.00	8.70	0.82	5.93
OeTPA-TRC	1.08	1.56	4.00	7.63	0.79	6.26
YD-TRC	1.28	1.47	1.22	4.65	0.55	208.59

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- 1. Six s-triazine based donor-acceptor systems were synthesized and characterized
- 2. These donor-acceptor systems have different lifetimes of charge separated states
- 3. The driving forces and reorganization energies of electron transfer determine the

lifetimes