Supporting information

A Photochromic Diarylethene Dyad Based on Perylene Diimide

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The distinguished absorbance contribution of each functional unit can be observed with the comparison of the absorption spectra of the open forms and photostationary states (PSS) in the supporting information. Although no distinct new absorption bands were detected, compared with those of DTE and PDI, the very slight red-shift observed for PDI-DTE indicate that the PDI and DTE units of PDI-DTE are strongly interacted in the ground state (Figure 2), which is consistent with the results of the calculation mentioned below.

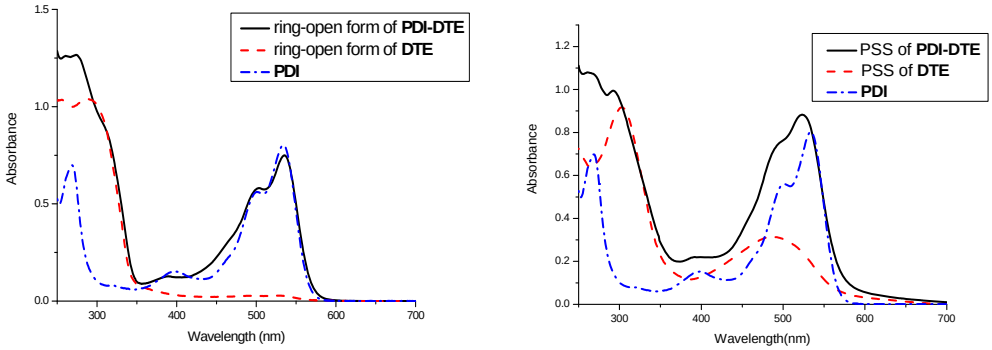


Fig. S1. UV-Vis absorption spectral difference of DTE, PDI, PDI-DTE (5×10^{-5} M) in THF at 298 K before and after irradiation with 254 nm UV light.

Time-dependent density functional theory (TDDFT) calculations are also performed by using the PBE0 functional and the 6-31G(d) basis set, to further investigate the excited states of the PDI-DTE. The TDDFT results are listed in Table 1. Two remarkable absorption bands are found for the open form of PDI-DTE, i.e., the S_1 and S_3 excited states corresponding to the absorption of 567 nm and 504 nm, respectively. For the closed form of PDI-DTE, the HOMO→LUMO transition has very low oscillator strength, and the main contributions to the absorption bands come from the S_3 and S_5 excited states. It should be noted that there is a significant energy gap between the S_1/S_2 and the $S_3/S_4/S_5$ excited states of PDI-DTE-closed, which prevents the internal conversion from the higher excited states to the lower excited states.

Table S1. Calculated TDDFT excitation energies for the lowest transition (eV, nm), oscillator strengths (*f*), and composition in terms of molecular orbital contributions.

Compounds	State	Composition [a]	E(eV, nm)	*f*
open	S_1	H→L(91%)	2.19, 566.9	0.3065
	S_2	H-1→L(96%)	2.26, 549.7	0.0211
	S_3	H-2→L(84%)	2.46, 504.4	0.4767
	S_4	H-3→L(94%)	2.77, 448.2	0.0189
	S_5	H-4→L(94%)	2.82, 439.8	0.0483
closed	S_1	H→L(96%)	1.42, 874.6	0.0848
	S_2	H-1→L(96%)	1.43, 866.4	0.0043
	S_3	H-2→L(36%) H-1→L+1(23%) H→L+2(22%)	2.34, 529.8	1.2582
	S_4	H→L+2(22%) H→L+1(20%) H-1→L+1(19%) H-1→L+2(17%)	2.41, 515.5	0.0319
	S_5	H-2→L(43%) H-1→L+1(18%) H→L+2(15%)	2.44, 507.9	0.3701

[a] H = HOMO, L = LUMO, H-1 = the next highest occupied molecular orbital, L+1 = the next lowest unoccupied molecular orbital, etc.

The fluorescence decay of compounds PDI-DTE and PDI in THF was recorded at 565 nm upon excitation at 440 nm. Time profiles of fluorescence intensities of both compounds were shown in Figure 3. In the case of **PDI-DTE (both open and closed form)**, the decays obeyed single exponential function giving a single fluorescence lifetime (τ = ~ 4 ns). On the other hand, the decay of PDI consisted of a slow decay component (τ^1 = 44.53 ns, 9.5%) and fast component (τ^1 = 6.37 ns, 90.5%). From the longer lifetime compared with , an appreciable decrease in the decay rate of PDI-DTE was observed. It indicates that there may be electron transfer or energy transfer when DTE was linked to PDI.

Table S2. The fluorescence life-time data of PI and ring-closed PDI-DTE

compund	τ^1[ns] (Rel %)	τ^2 [ns] (Rel %)	χ^2
PDI	44.53(9.46)	6.37(90.54)	1.194
PDI-DTE(open form)	4.37(100)		1.161
PDI-DTE(closed form)	4.55(100)		1.103

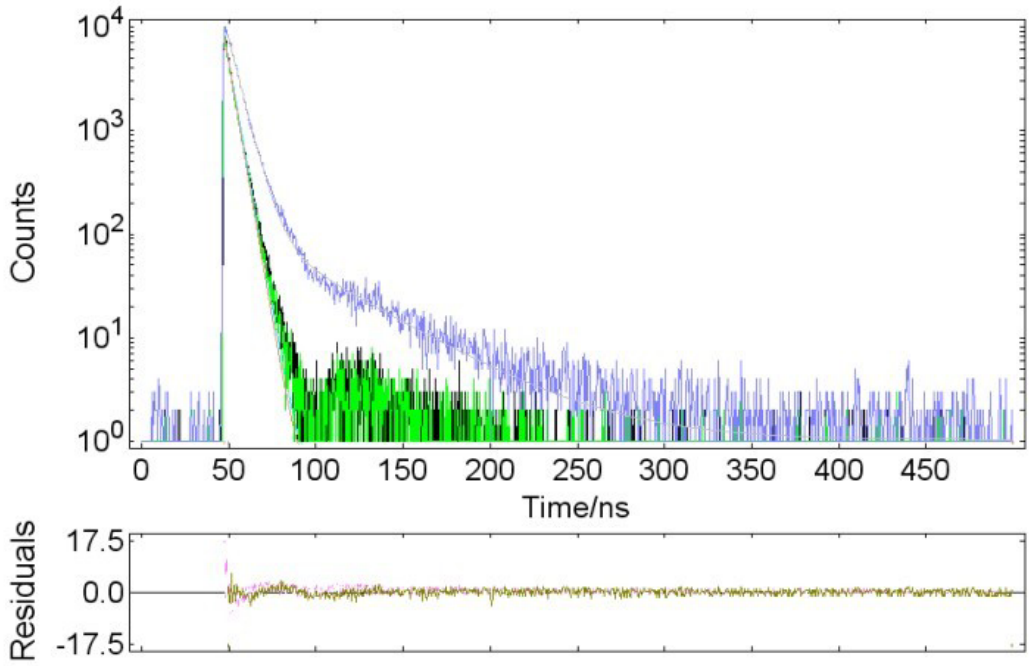
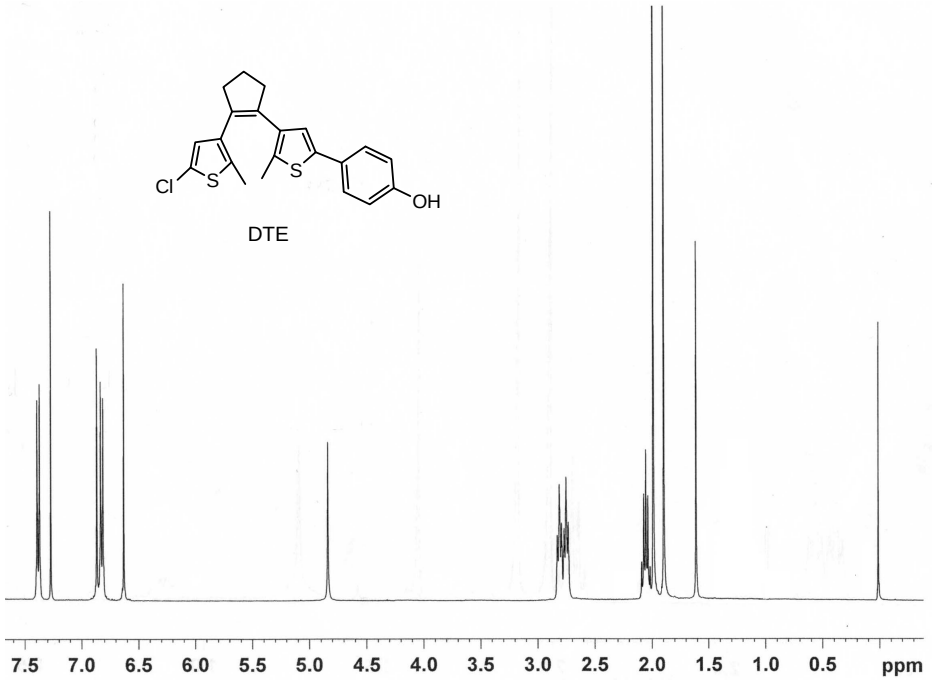
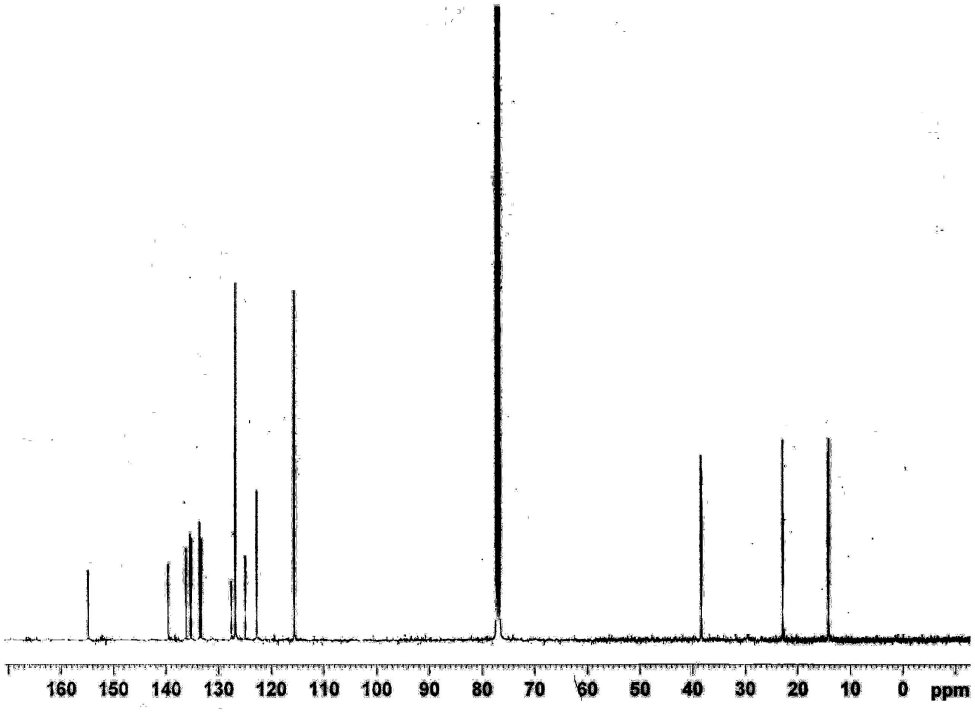


Fig. S2. The fluorescence life-time of PDI and the closed form of PDI-DTE was measured at 565 nm emission monitor upon excited at 440 nm.

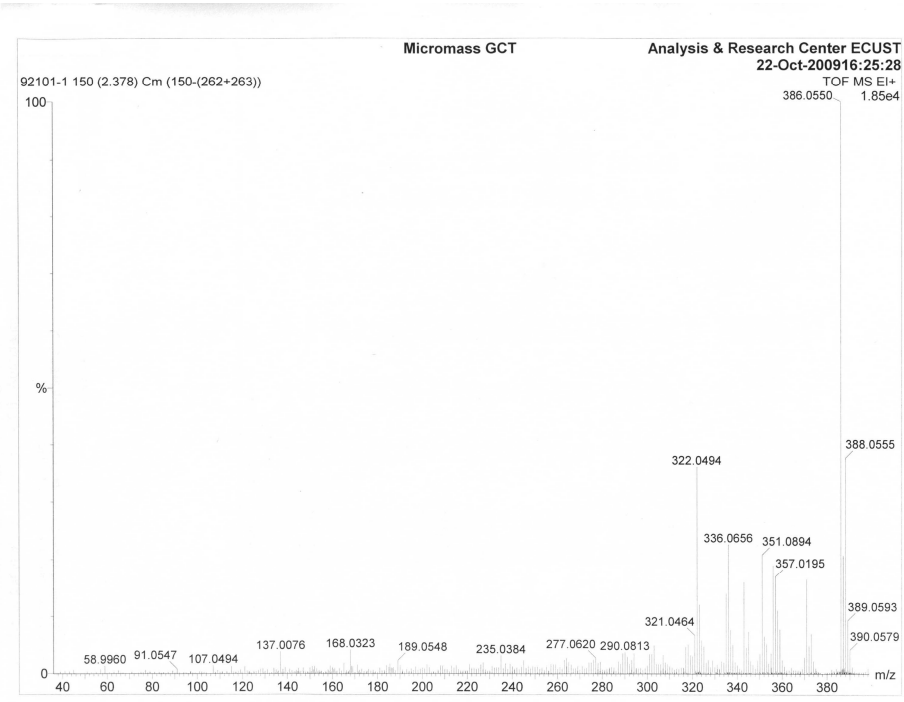
^{1}H NMR spectrum of DTE in $CDCl_3$ (400MHz)



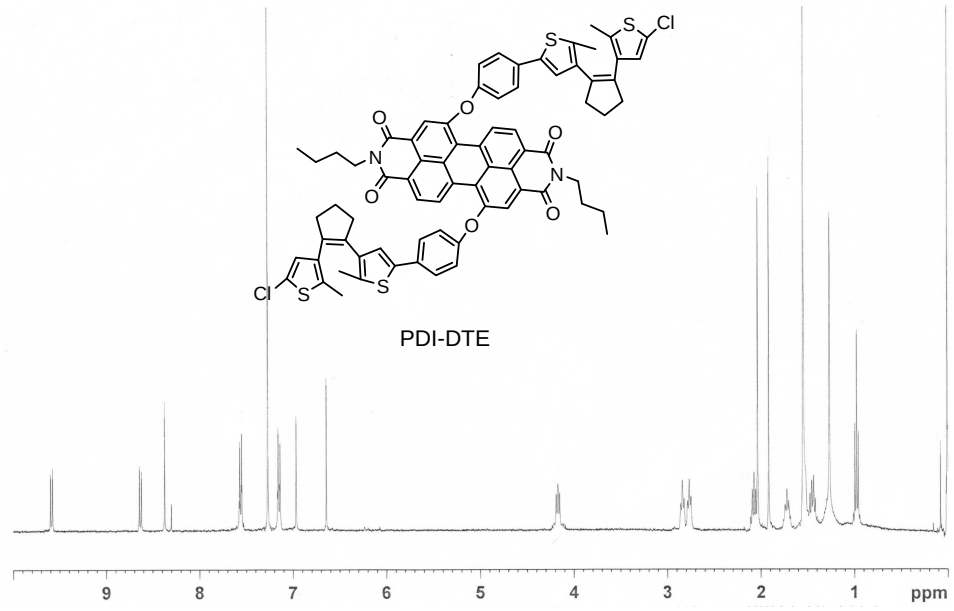
^{13}C NMR spectrum of DTE in $CDCl_3$ (400MHz)



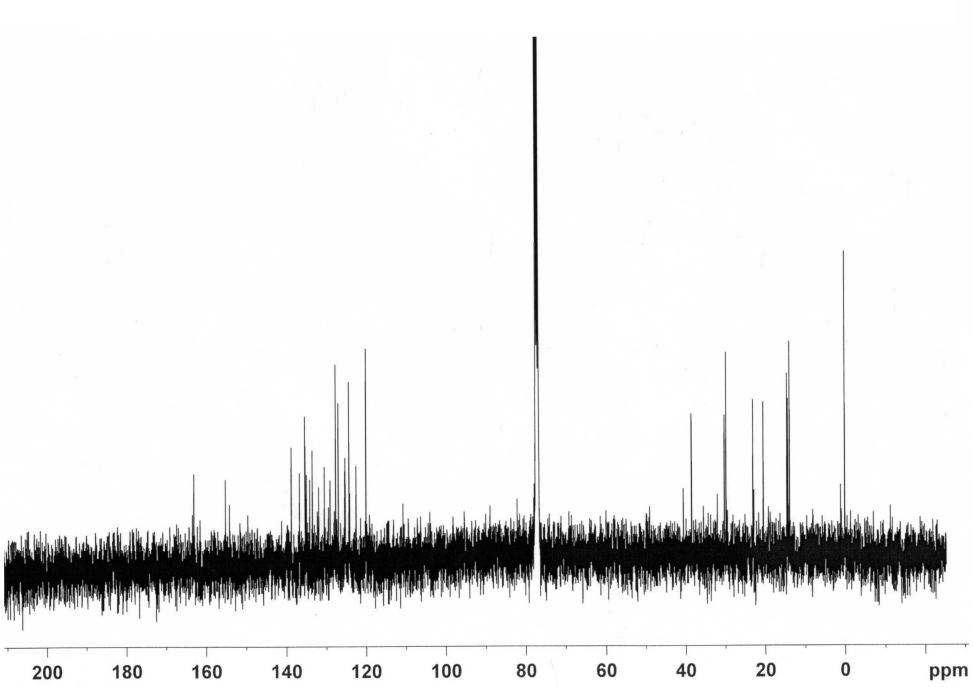
HRMS spectrum of DTE



^{1}H NMR spectrum of PDI-DTE in $CDCl_3$ (400MHz)



^{13}C NMR spectrum of PDI-DTE in $CDCl_3$ (400MHz)



MOLDI-TOF of PDI-DTE