Visible light-induced highly selective transformation of olefin to ketone by 2,4,6-triphenylpyrylium cation encapsulated within zeolite Y

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Electronic Supplementary Information (ESI†)



Fig. S1 (a) UV-vis absorption spectrum of TPT (5×10^{-4} M) dissolved in CH₂Cl₂ and (b) diffuse reflectance UV-vis spectrum of TPY.



Fig. S2 Thermogravimetrical profile of TPY (heating rate: 10 K/min).



Fig. S3 Relationship between average molecular diameter of olefins, (l + w)/2, and the ratio of $k_q(\text{TPY})/k_q(\text{TPT})$.



Fig. S4 Fluorescence decays of TPT dissolved in MeCN and of TPY suspended in MeCN, measured at 298 K ($\lambda_{ex} = 417 \text{ nm}$; $\lambda_{det} = 468 \text{ nm}$).

substrata	$E_{1/2}^{\operatorname{ox} b}$	$\Delta G^{\circ c}$	$k_{\rm q}$ / L mol ⁻¹ s ⁻¹			
substrate	/ V	/ kJ mol ⁻¹	TPT^{d}	TPY ^e	TPT+Y	
styrene (1)	1.94	-57.9	1.8×10^{10}	2.9×10^{9}	2.8×10^{10}	
α -methylstyrene (5)	1.64	-86.8	3.7×10^{10}	3.4×10^{9}	2.3×10^{10}	
1,1-diphenylethylene (9)	1.81	-70.4	4.7×10^{10}	3.1×10^{9}	2.2×10^{10}	
4-chloromethylstyrene (14)	1.95	-56.9	$2.7 imes 10^{10}$	$2.8 imes 10^9$	$2.0 imes 10^{10}$	
4-chlorostyrene (17)	2.09	-43.4	3.5×10^{10}	3.2×10^{9}	1.9×10^{10}	
<i>cis</i> -stilbene (20)	1.61	-89.7	2.2×10^{10}	1.4×10^{9}	1.2×10^{10}	
trans-stilbene (21)	1.49	-101.3	$6.7 imes 10^{10}$	3.3×10^{9}	4.2×10^{10}	
trans- β -methylstyrene (24)	1.71	-80.1	$1.7 imes 10^{10}$	1.7×10^{9}	$1.4 imes 10^{10}$	

Table S1. Oxidation potential of olefins, fluorescence quenching rate constant, k_q ,^{*a*} and free energy change associated with ET from olefin to the singlet excited-state sensitizers

^{*a*} λ_{ex} = 417 nm; λ_{det} = 468 nm. ^{*b*} *vs.* Ag/AgCl (in MeCN with TBA·BF₄⁻). ^{*c*} estimated according to the Rehm–Weller equation ΔG° = 96.48 [$E(D^+/D) - E(A/A^-) - E_{0,0} + e_0^2/\epsilon a$],^{S1} where $E(A/A^-)$ for TPT (TPY) is –0.26 V; $E_{0,0}$ = 2.8 eV;^{S2} the final $e_0^2/\epsilon a$ term can be ignored since TPT (or TPY) is positively charged, and hence there is no net change in charge upon ET.^{S2} ^{*d*} fluorescence lifetime of TPT dissolved in MeCN at 298 K is 4.5 ns (see Fig. S4). ^{*d*} fluorescence lifetime of TPY, when suspended in MeCN, is 4.0 ns at 298 K (see Fig. S4).

·,·	substrate	product distribution / %					
sensitizer	conv / %	ketone	1	others	hers		
		2^{-0}	21	22 0 22	23		
TPY	4.1	trace	>99	0	trace		
TPT	46.6	10	79	10	1		
	21	2 ⁼⁰		22 0 22	23		
TPY	10.2	6	94	0	trace		
TPT	33.8	25	57	18	trace		
	24	2 ⁻⁰	25		26 ²		
TPY	5.0	50	50		trace		
TPT	16.9	65	16		19		

Table S2. Product distribution in the photooxygenation of β -substituted styrenes on TPY and TPT^{*a*}

^{*a*} The reaction conditions are the same as Table 1.

References

- (S1) D. Rehm and A. Weller, Isr. J. Chem., 1970, 8, 259.
- (S2) R. Akaba, H. Sakuragi and Tokumaru, J. Chem. Soc., Perkin Trans. 2, 1991, 291.