Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Conjugated phenothiazinyl Oxime esters as free radical photoinitiators

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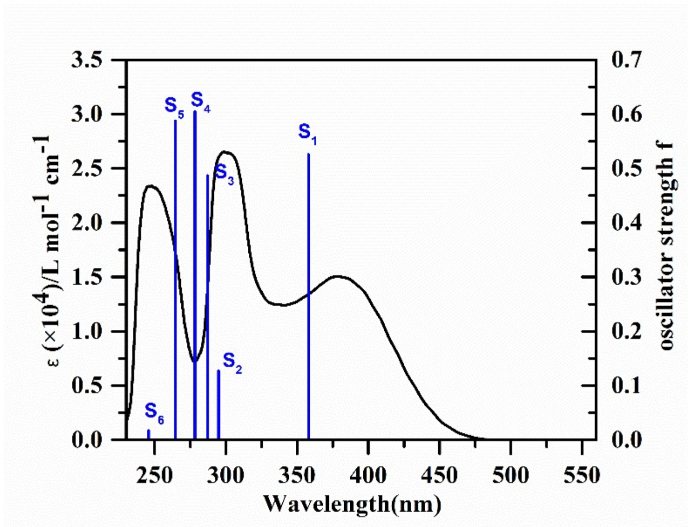


Fig. S1 Experimental UV−vis spectra calculated excited singlet states (blue) of Ph-PTZ-OXE

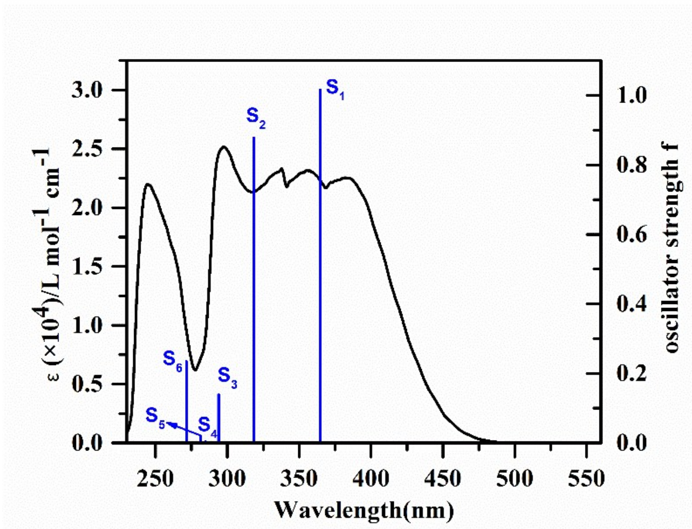


Fig. S2 Experimental UV−vis spectra calculated excited singlet states (blue) of TPA-PTZ-OXE

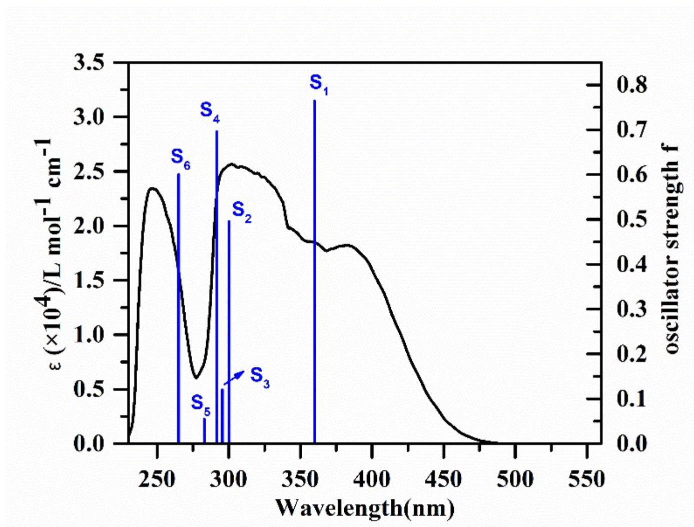


Fig. S3 Experimental UV−vis spectra calculated excited singlet states (blue) of CZ-PTZ-OXE

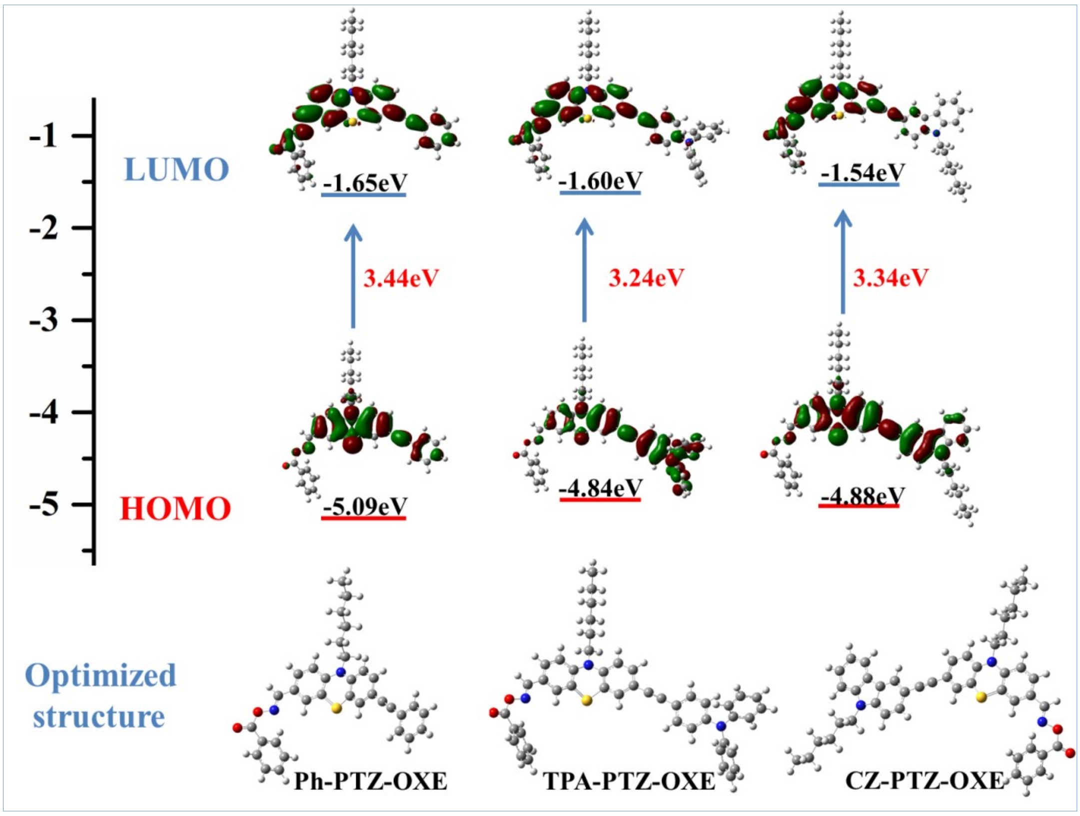


Fig. S4 Optimized geometry, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE at the B3LYP/6-31G* level.

Table S1 Data on the electron transition of oxime ester molecules

Molecule	states	E (eV)	λ(nm)	f_{os}	Main contribution	
Ph-PTZ-OXE	1	3.465	357.82	0.5258	HOMO →LUMO	0.842532
	2	4.2078	294.65	0.1266	HOMO →LUMO+1	0.453285
TPA-PTZ-OXE	1	3.4026	364.38	1.0159	HOMO →LUMO	0.597543
	2	3.8972	318.14	0.8781	HOMO →LUMO+1	0.418576
CZ-PTZ-OXE	1	3.4471	359.67	0.7637	HOMO →LUMO	0.693135
	2	4.1321	300.05	0.4954	HOMO →LUMO+1	0.390392

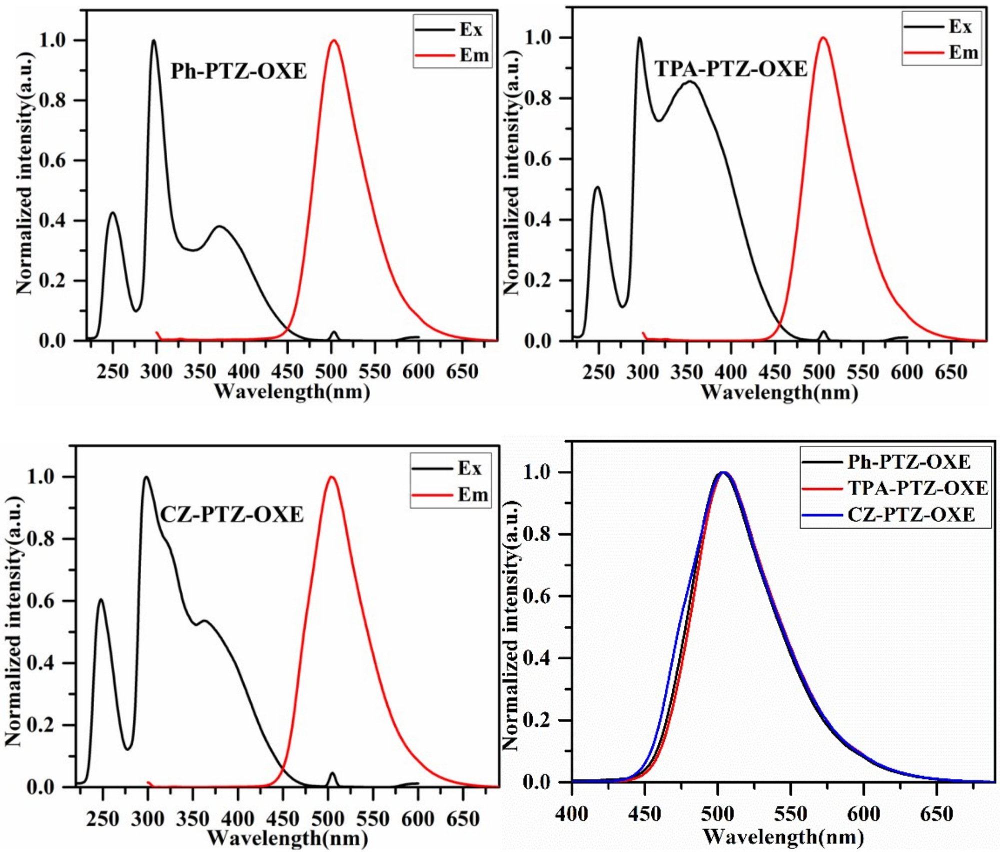


Fig. S5 Normalized fluorescence excitation and emission spectra of Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE in THF solution (M=1 × 10^{-5} mol L^{-1}); (2) Normalized fluorescence emission spectra of oxime esters in THF solution (M=1 × 10^{-5} mol L^{-1}).

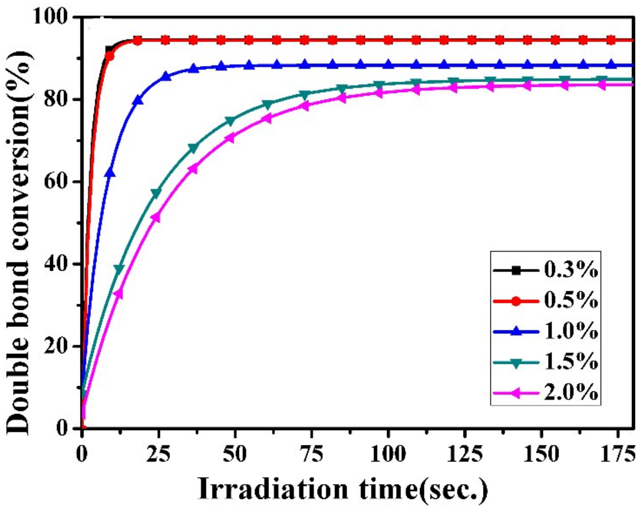


Figure S6. Photopolymerization profiles of TPGDA in the presence of OXE (TPGDA: 100 wt%; OXE: 0.2%,ONI:0.5%,1.0%1.5%,2.0%) under the laser diode at 405 nm

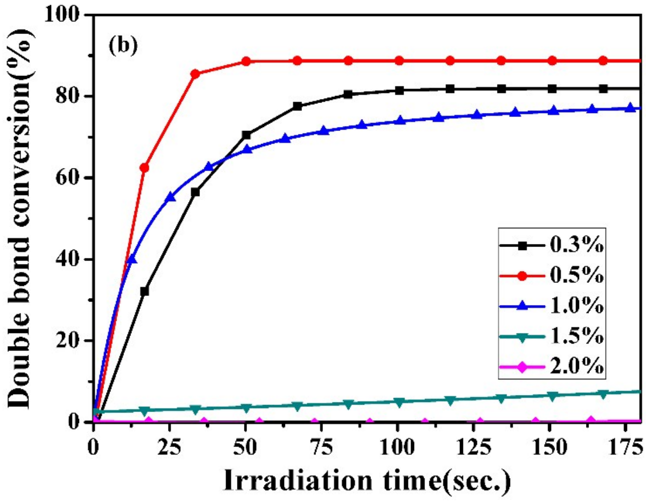
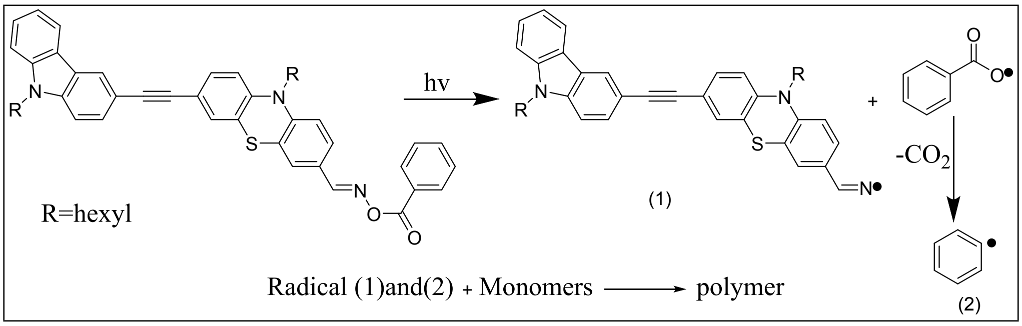


Figure S7. Photopolymerization profiles of TPGDA in the presence of OXE (TPGDA: 100 wt%; OXE: 0.2%,ONI:0.5%,1.0%1.5%,2.0%) under the laser diode at 455 nm.



Scheme S1. Initiation mechanism of oxime ester photoinitiator

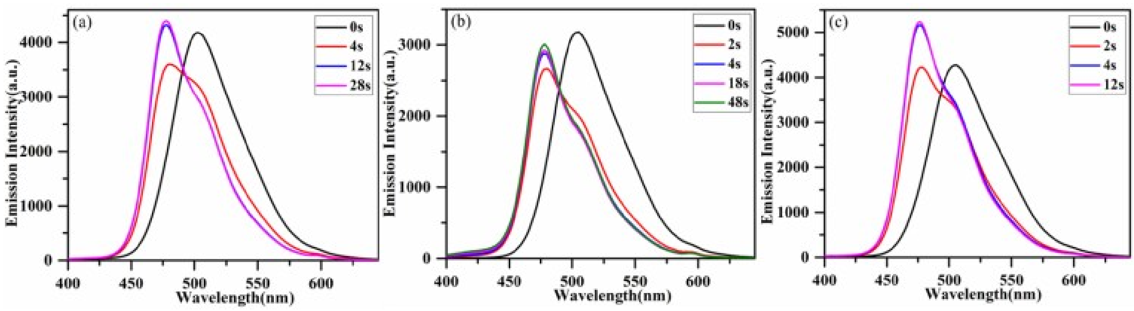


Fig. S8. Fluorescence spectra of OXE in THF solution under the laser diode at 405 nm exposure at different irradiation times (M=1 × 10^{-5} mol L^{-1}): (a) Ph-PTZ-OXE, (b) TPA-PTZ-OXE, (c) CZ-PTZ-OXE

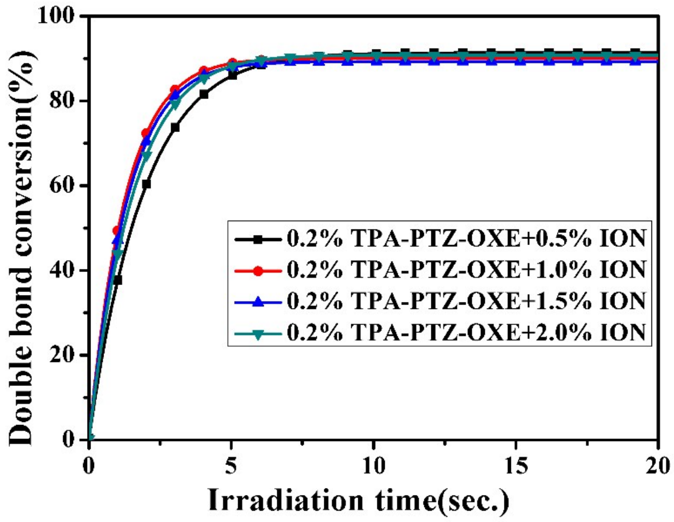


Fig. S9. Photopolymerization profiles of TPGDA in the presence of OXE (TPGDA: 100 wt%; OXE: 0.2%,ONI:0.5%,1.0%1.5%,2.0%) under the laser diode at 405 nm

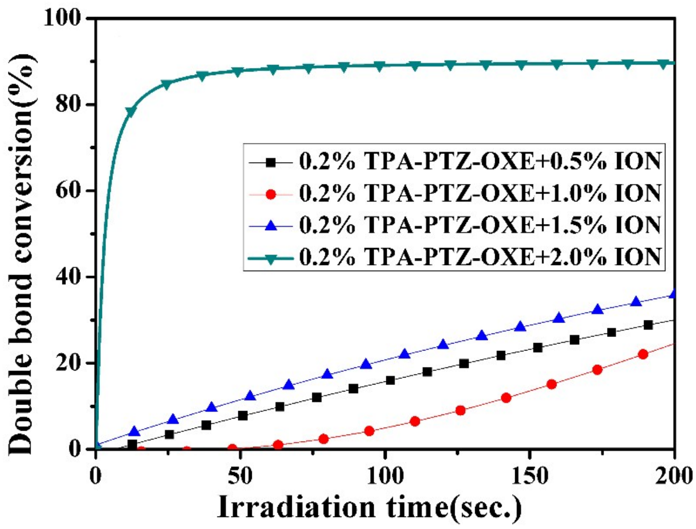


Fig. S10. Photopolymerization profiles of TPGDA in the presence of OXE (TPGDA: 100 wt%; OXE: 0.2%,ONI:0.5%,1.0%, 1.5%,2.0%) under the laser diode at 455 nm

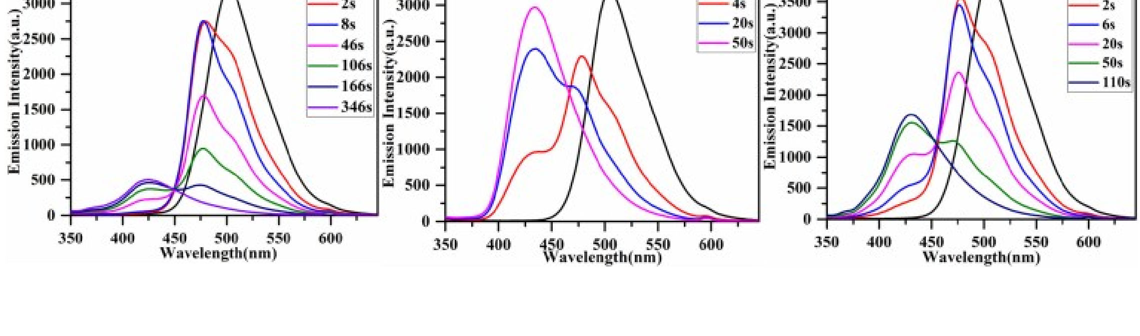
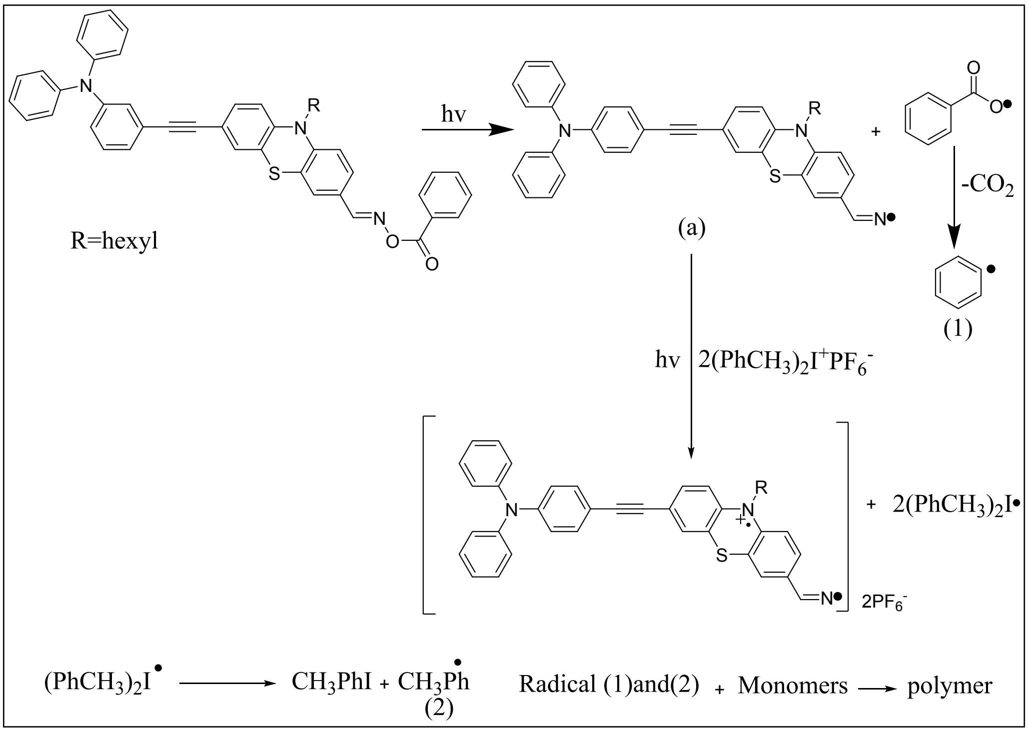


Fig. S11 Fluorescence spectra of OXE/ION systems in THF solution under the laser diode at 405 nm exposure at different irradiation times (M_{OXE}=1 × 10^{-5} mol L^{-1}, M_{ION}=1 × 10^{-3} mol L^{-1}, m_{OXE} : m_{ION} = 1 : 10): Ph-PTZ-OXE/ION (a), TPA-PTZ-OXE/ION (b), CZ-PTZ-OXE/ION (c)



Scheme S2. Mechanism of OXE / ION photoinitiating system

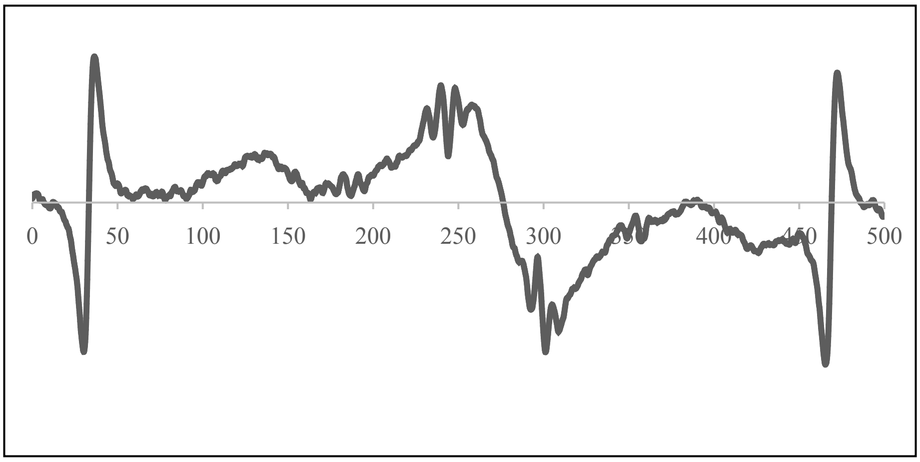


Fig. S12. ESR spectra of the radicals generated in TPA-PTZ-OXE/ION in TPGDA

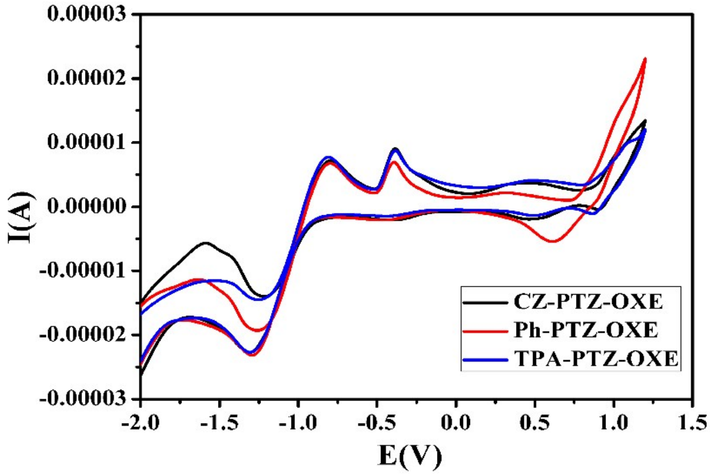


Fig. S13 Cyclic voltammogram curves of Ph-PTZ-OXE, TPA-PTZ-OXE and PTZ-PTZ-OXE in THF (Mdye = $1.01 \times 10{-}3$ mol L^{-1}).

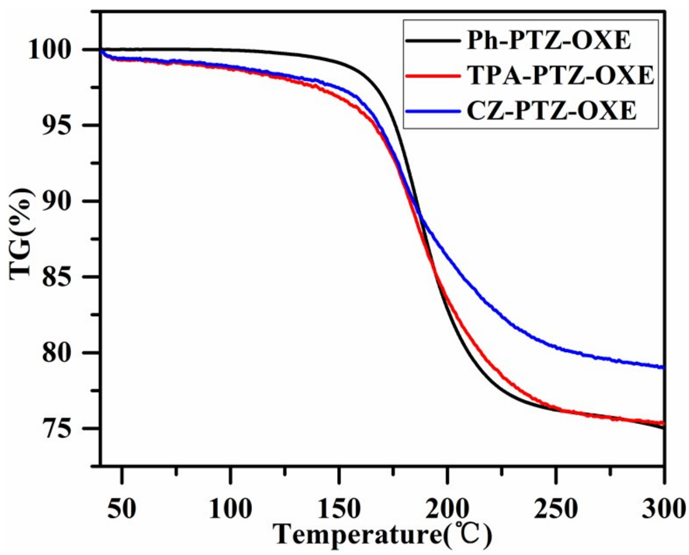


Fig. S14 Thermal gravimetricand curves of oxime esters

Table S2 Temperature of oxime esters mass loss

OXE	$T_{initial}$(°C)	T_{max}(°C)	$T_{finally}$(°C)
Ph-PTZ-OXE	140	190	290
TPA-PTZ-OXE	120	190	300
CZ-PTZ-OXE	130	185	300