Supporting Information

Thiophene-Substituted Phenothiazine-Based Photosensitisers for Radical and Cationic Photopolymerizations Reaction under Visible Laser Beams (405 and 455nm)

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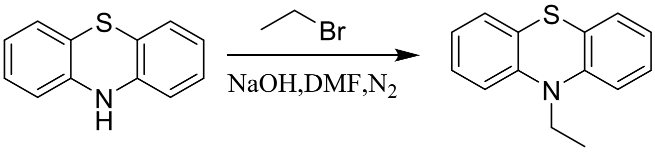
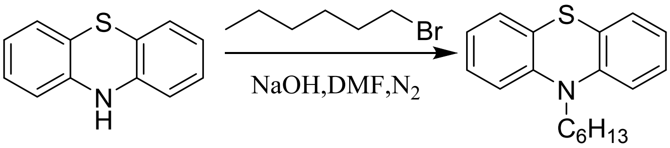
1. Synthesis of EPTZ[1, 2]



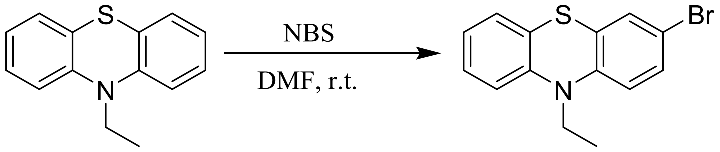
Yield: 95.15%; ^{1}H NMR (400 MHz, CDCl3) δ 7.20 (dd, *J* = 12.5, 6.5 Hz, 4H), 6.93 (dd, *J* = 18.4, 7.7 Hz, 4H , 3.96 (q, *J* = 6.78 Hz, 2H), 1.45 (t, *J* = 7.03 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 145.03, 127.39, 127.24, 124.49, 122.35, 115.15, 41.78, 13.07.

2. Synthesis of HPTZ [3]



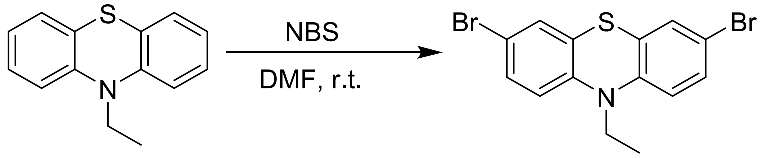
Yield: 82.33%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (t, *J* = 7.58 Hz, 1H), 6.92 (dd, *J* = 18.7, 7.7 Hz, 1H), 3.87 (t, *J* = 6.8, 2H), 1.83 (m, 2H), 1.50–1.42 (m, 2H), 1.36–1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.29, 127.42, 127.17, 124.93, 122.35, 115.44, 60.40, 47.50, 31.48, 26.69, 22.60, 14.00.

3. Synthesis of MBrEPTZ [2, 4, 5]



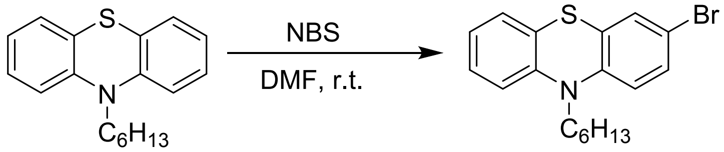
Yield: 74.37%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.75 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.87 (d, *J* = 8.08 Hz, 1H), 6.72 (d, *J* = 9.07 Hz, 1H), 3.87 (q, *J*=7.6, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz,CDCl$_3$) δ130.16, 129.85, 129.67, 129.55, 127.49, 126.84, 123.80, 122.67, 116.34, 116.22, 115.24, 114.45, 41.89, 12.91.

4. Synthesis of DBrEPTZ[6]



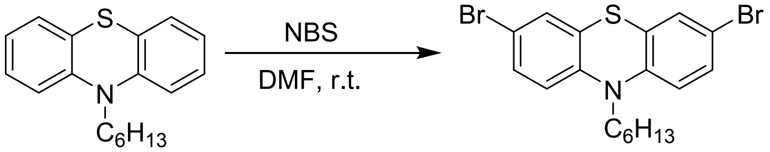
Yield: 68.76%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, *J* = 2.3 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.84 (q, *J* = 6.85 Hz, 2H), 1.39 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.76, 130.15, 129.62, 125.94, 116.34, 114.76, 42.05, 12.80.

5. Synthesis of MBrHPTZ [7]



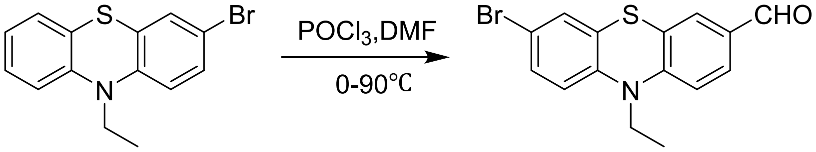
Yield: 80.11%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (dq, *J* = 4.0, 2.2 Hz, 2H), 7.16 (ddd, *J* = 9.0, 8.1, 1.3 Hz, 2H), 6.92 (dd, *J* = 29.0, 7.5 Hz, 2H), 6.71 (dd, *J* = 8.2, 4.9 Hz, 1H), 3.79 (q, *J* = 6.9 Hz, 2H), 1.84–1.74 (m, 2H), 1.49–1.40 (m, 2H), 1.36–1.29 (m, 4H), 0.90 (t, *J* =7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 130.12, 129.83, 129.73, 129.63, 127.45, 127.30, 126.48, 122.68, 116.67, 116.56, 115.57, 114.76, 47.64, 31.41, 26.59, 26.51, 22.59, 13.99.

6. Synthesis of DBrHPTZ



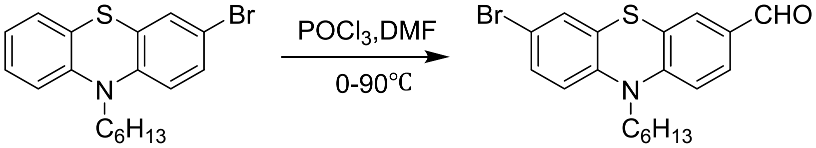
Yield: 61.53%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 3H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.78 (q, *J* = 6.9 Hz, 2H), 1.76 (m, 2H), 1.41 (m, 2H), 1.33–1.28 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.13, 130.12, 129.71, 126.49, 116.67, 114.78, 47.62, 31.38, 26.66, 26.50, 22.57, 13.98.

7. Synthesis of MBrFEPTZ [8, 9]



Yield: 79.65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.66 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.29–7.25 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 3.96 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.88, 149.85, 142.29, 131.26, 130.36, 130.26, 129.70, 128.29, 125.60, 123.82, 116.68, 115.81, 114.58, 42.59, 12.73.

8. Synthesis of MBrFHPTZ



Yield: 77.41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.67 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.29–7.24 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 3.89–3.84 (m, 2H), 1.81 (m, 7.4 Hz, 2H), 1.44 (m, 2H), 1.37–1.28 (m, 4H), 0.90 (t, *J* = 7.0, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.90, 150.34, 142.67, 131.30, 130.24, 129.80, 128.46, 127.56, 126.17, 124.41, 117.09, 115.81, 115.00, 48.10, 31.34, 26.62, 26.44, 22.55, 13.96.

Table S1. Optical absorption properties of the dyes ThPTZs (5×10^{-5} mol/L)

Dyes	λ_{max} (nm)	$\varepsilon_{max}\times10^{4}$ ($M^{-1}\cdot cm^{-1}$)	λ_{max} (nm)	$\varepsilon_{max}\times10^{4}$ ($M^{-1}\cdot cm^{-1}$)	$\varepsilon_{max2}\times10^{3}$ ($M^{-1}\cdot cm^{-1}$)(405nm)	$\varepsilon_{max2}\times10^{3}$ ($M^{-1}\cdot cm^{-1}$)(455 nm)
ThEPTZ	**307.7**	**3.18**	**363.3**	**0.87**	**3.37**	**0.33**
Th_2EPTZ	**317.6**	**4.69**	**375.4**	**1.26**	**8.87**	**1.86**
ThFEPTZ	**327.7**	**9.93**	**435.4**	**1.02**	**6.93**	**9.19**
ThHPTZ	**308.3**	**2.82**	**363.4**	**0.76**	**2.88**	**0.33**
Th_2HPTZ	**317.5**	**4.02**	**375.4**	**1.11**	**7.58**	**1.51**
ThFHPTZ	**327.4**	**3.54**	**435.4**	**0.94**	**6.37**	**8.36**

Table S2. Epoxy conversions of E51 in a laminate obtained under air upon exposure to different visible laser diodes for 300 s and final conversion (Cf) in the presence of ThPTZs/ION (0.1%: 3.0%, w/w); And EPTZ/ION (0.1%: 3.0%, w/w) as references.

ThPTZs/ION	**Epoxy Conversion (%) for E51**			
	405 nm		**455 nm**	
	300 s	**Cf**	**300 s**	**Cf**
ThEPTZ/ION	58.2	62.3	62.8	64.1
ThHPTZ/ION	56.5	60.8	64.4	65.6
Th2EPTZ/ION	70.5	72.2	68.5	70.2
Th2HPTZ/ION	67.5	69.4	69.2	70.9
ThFEPTZ/ION	67.1	68.7	71.4	72.8
ThFHPTZ/ION	65.8	67.3	72.7	74.7
EPTZ/ION	14.7	20.3	15.9	21.4

Table S3. Double bond conversions of TPGDA in a laminate obtained under air upon exposure to different visible laser diodes for 100 and 200 s in the presence of ThPTZs/ION (0.1%/1.0%, w/w); EPTZ/ION (0.1%/1.0%, w/w), CQ/TEA (0.1%/10%, w/w) and ION as references.

ThPTZs/ION	**Double Conversion (%) for TPGDA**			
	405 nm		**455 nm**	
	100 s	**200 s**	**100 s**	**200 s**
ThEPTZ/ION	**44.7**	**62.5**	**39.4**	**73.6**
ThHPTZ/ION	**39.9**	**57.8**	**32.4**	**71.8**
Th2EPTZ/ION	**74.9**	**80.7**	**79.6**	**79.8**
Th2HPTZ/ION	**69.8**	**80.0**	**79.9**	**80.5**
ThFEPTZ/ION	**76.1**	**77.1**	**82.1**	**82.0**
ThFHPTZ/ION	**78.2**	**78.9**	**83.5**	**83.5**
EPTZ/ION	**7.9**	**15.4**	**11.3**	**18.8**

CQ/TEA	**12.2**	**20.1**	**14.2**	**22.8**

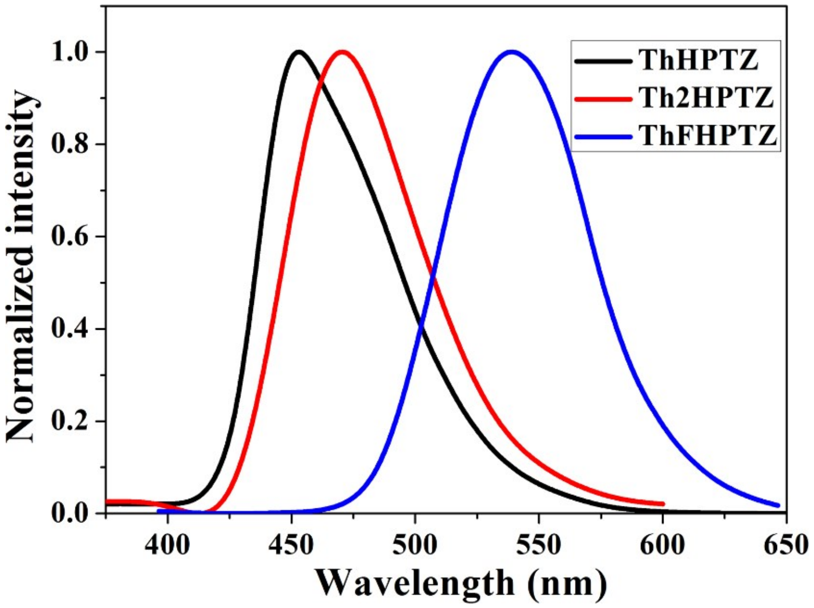


Figure S1. Normalized fluorescence emission spectra of the other dyes in DMF solution (M=5×10^{-5} mol/L).

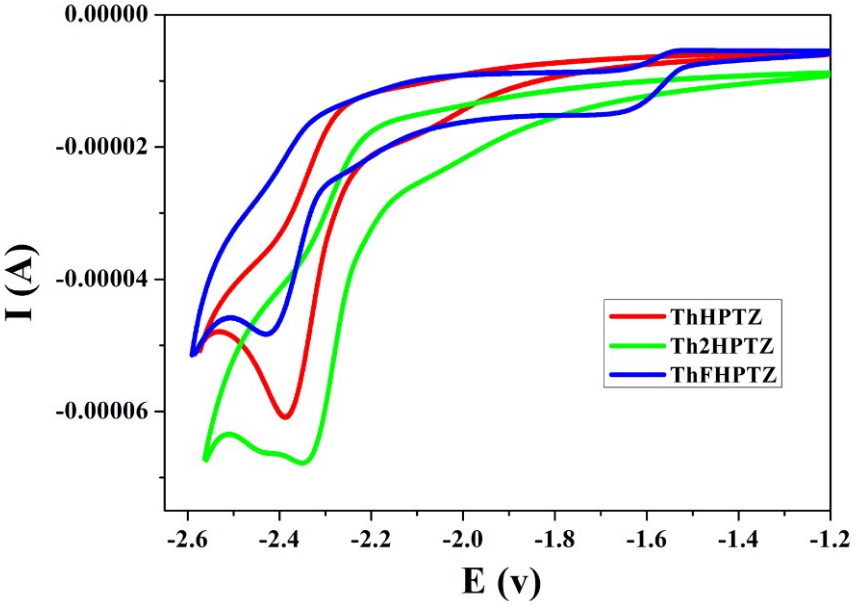


Figure S2. Cyclic voltammogram curves of ThHPTZ, Th2PTZ and ThFHPTZ in DCM

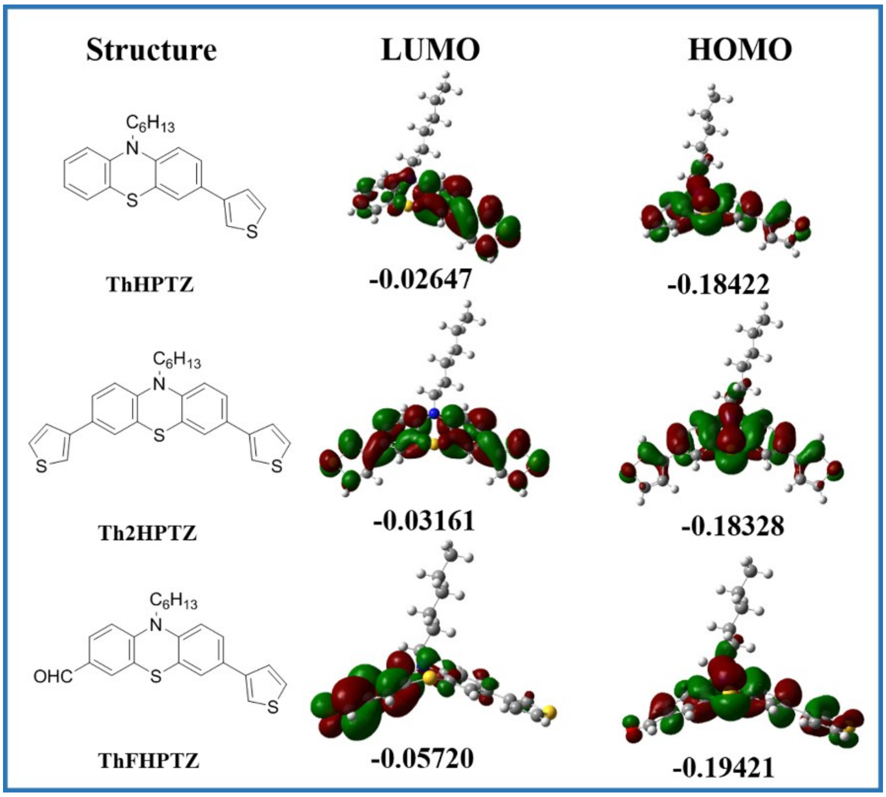


Figure S3. Optimized geometry, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of ThHPTZ, Th2HPTZ and ThFHPTZ at the B3LYP/6-31G* level.

References

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