Cyanine/iodonium salt as a broad-absorbing photoinitiating systems for radical photopolymerization under near-UV, visible and NIR lights

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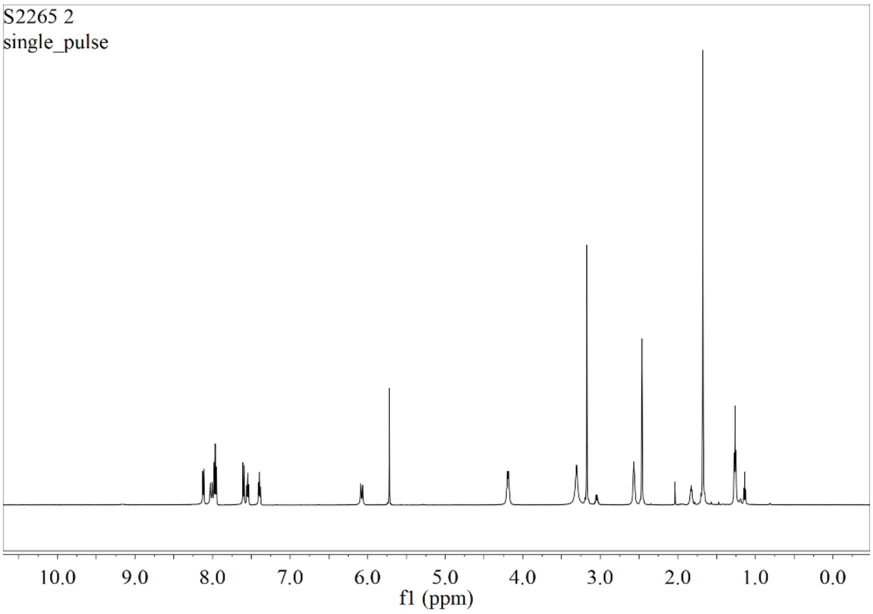

Fig. S1 ^{1}H NMR spectrum of S2265.

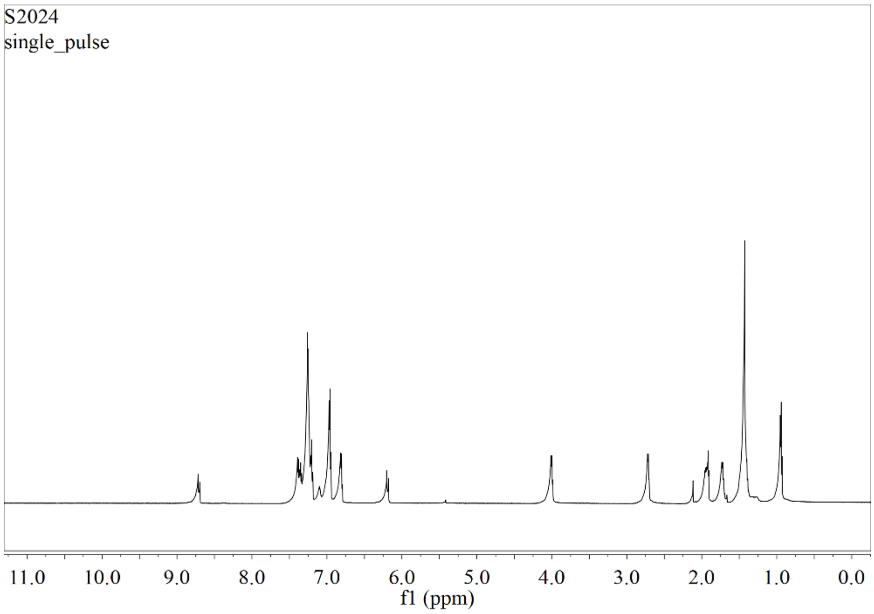

Fig. S2 [1]H NMR spectrum of S2024.

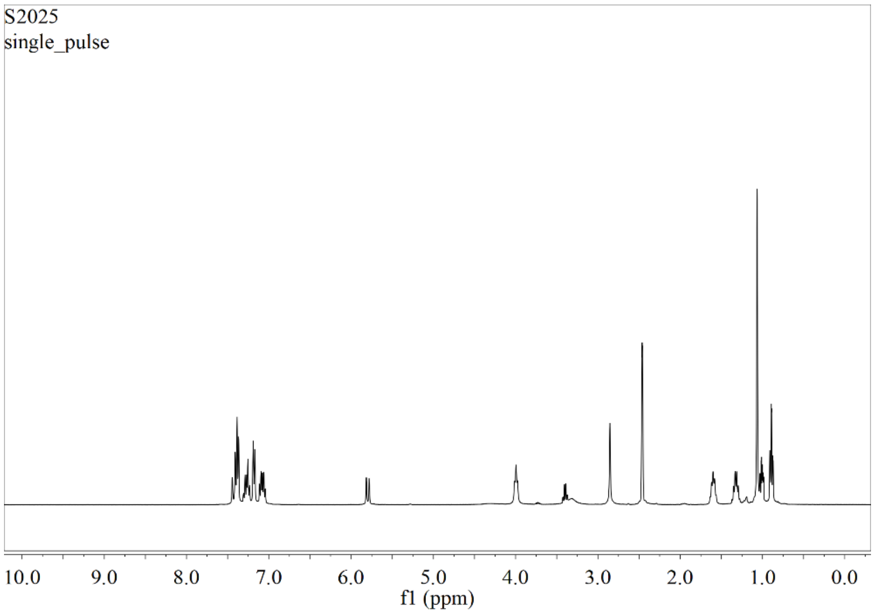

Fig. S3 [1]H NMR spectrum of S2025.

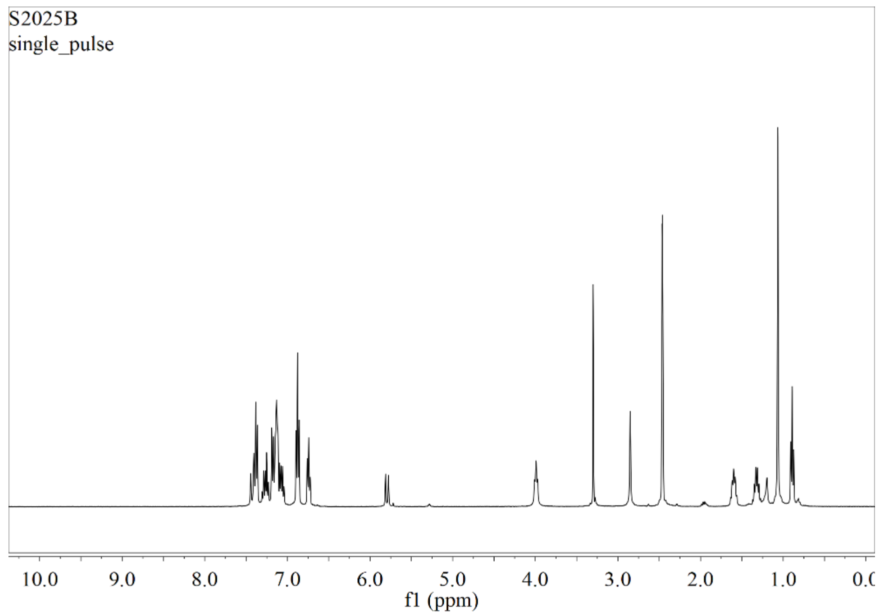

Fig. S4 ^{1}H NMR spectrum of S2025B.

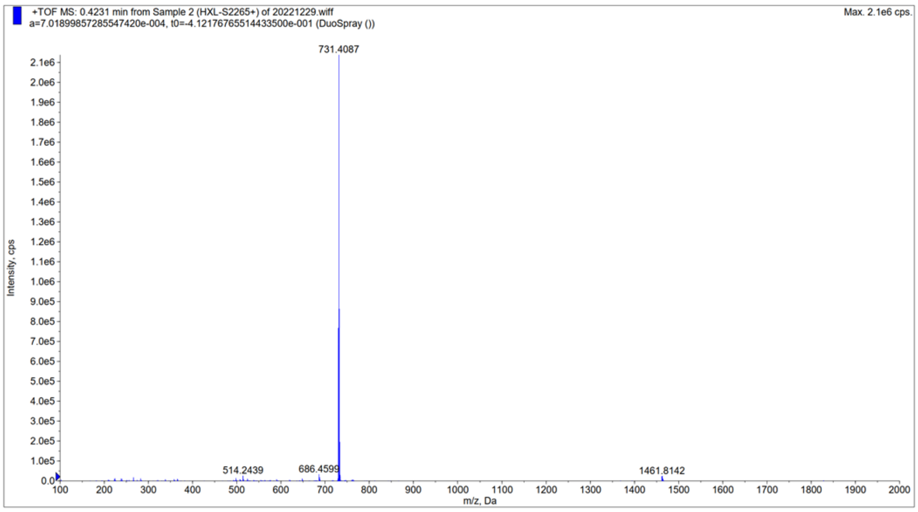

Fig. S5 High-resolution mass spectra (HRMS) of S2265.

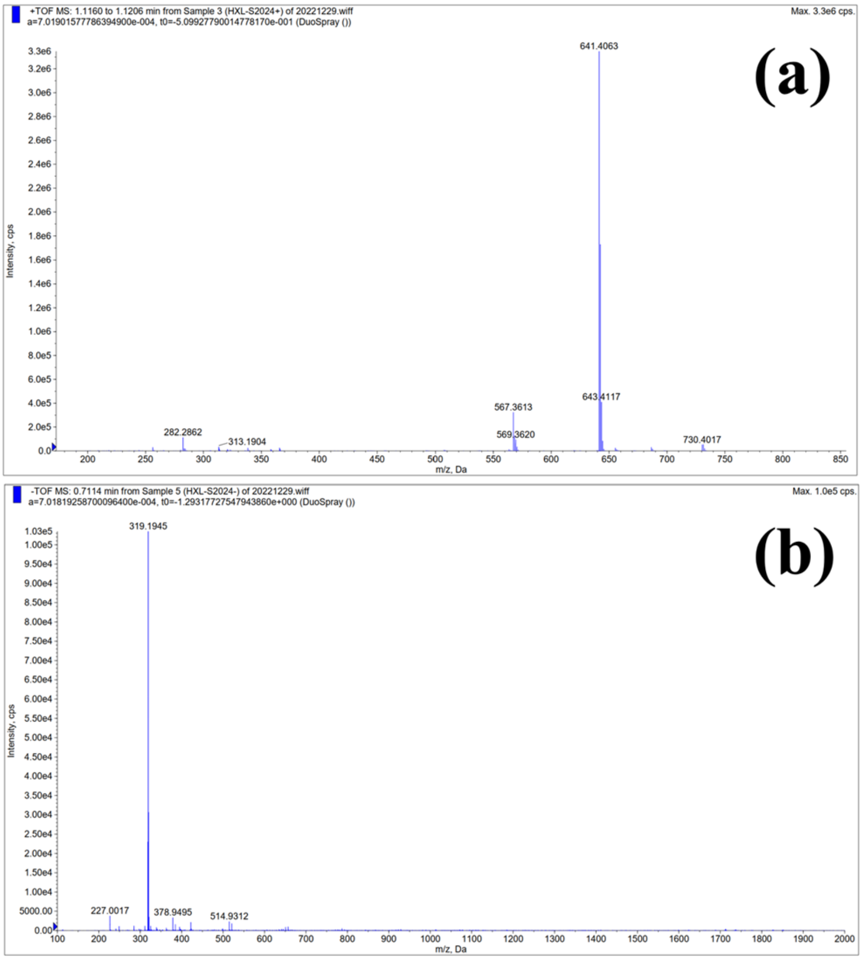

Fig. S6 High-resolution mass spectra (HRMS) of S2024, M^+ for (a) and M^- for (b).

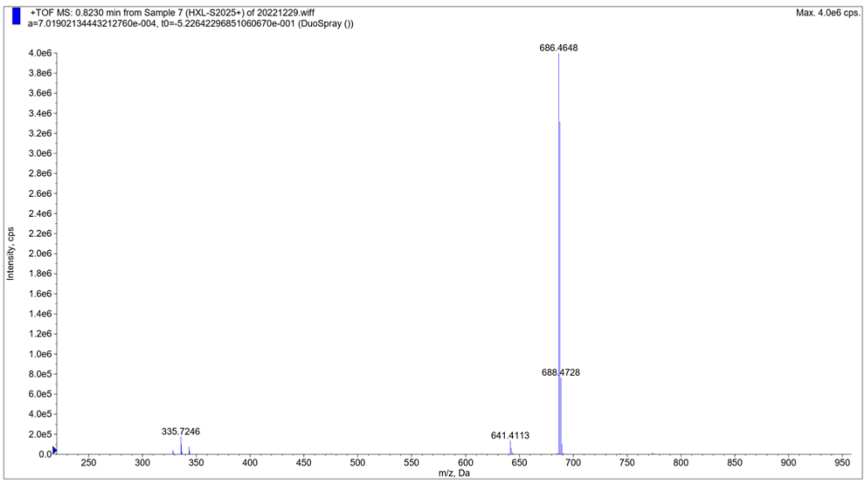

Fig. S7 High-resolution mass spectra (HRMS) of S2025 (M^+).

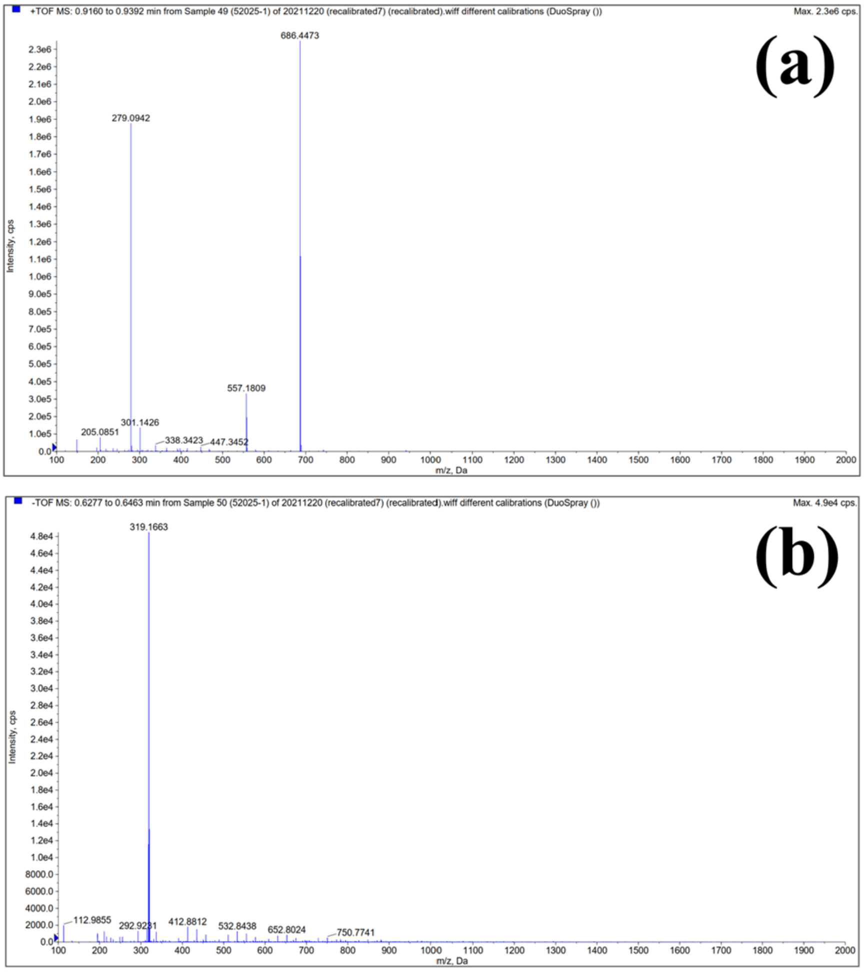

Fig. S8 High-resolution mass spectra (HRMS) of S2025B, M^+ for (a) and M^- for (b).

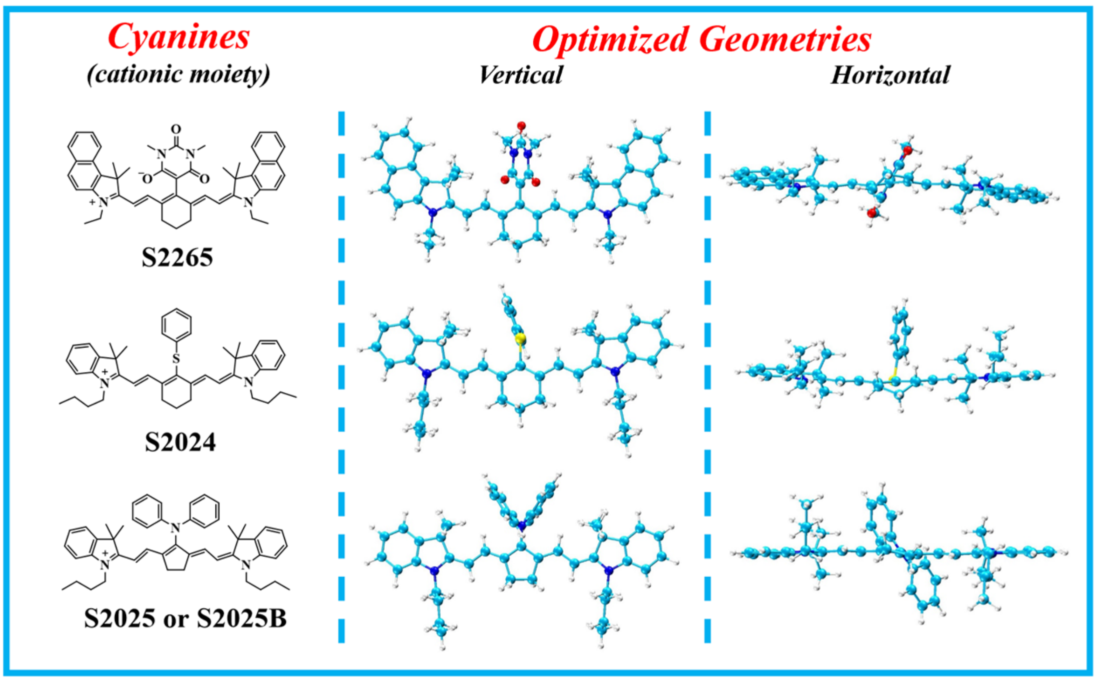

Fig. S9 Optimized geometries of cyanines (cationic moiety) at B3LYP/6-31G* level.

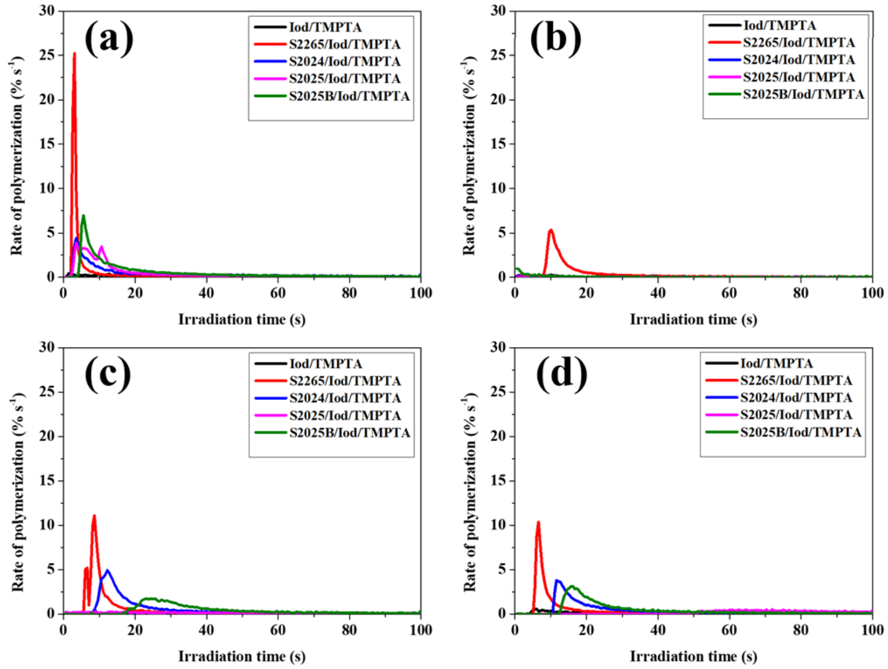

Fig. S10 Photopolymerization rate of cyanine/Iod/TMPTA systems (0.002:0.01:1, mole ratio) upon irradiation at (a) 808 nm laser, (b) 630 nm LED, (c) 450 nm LED and (d) 400 nm UV-LED.

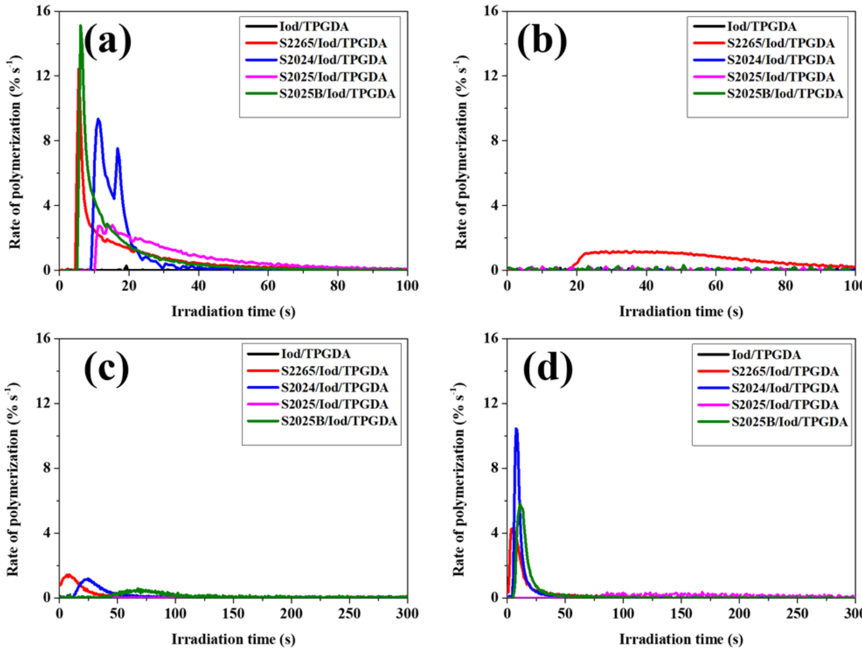

Fig. S11 Photopolymerization rate of cyanine/Iod/TPGDA systems (0.002:0.01:1, mole ratio) upon irradiation at (a) 808 nm laser, (b) 630 nm LED, (c) 450 nm LED and (d) 400 nm UV-LED.

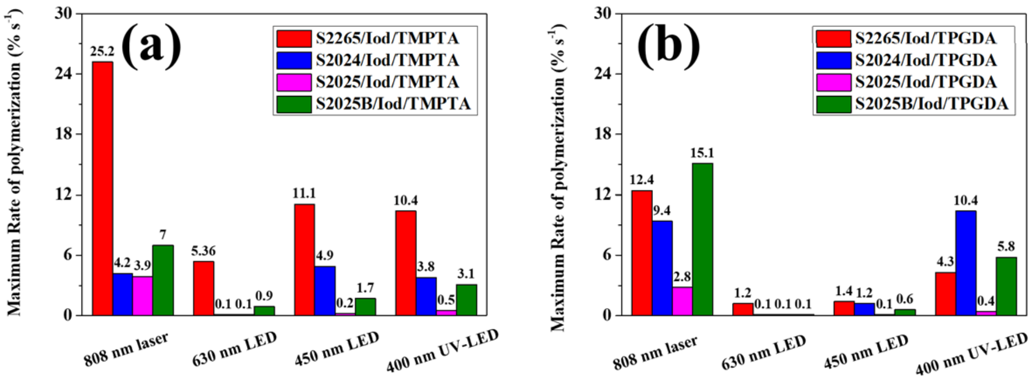

Fig. S12 Maximum rates of polymerization for cyanine/Iod/monomer systems.

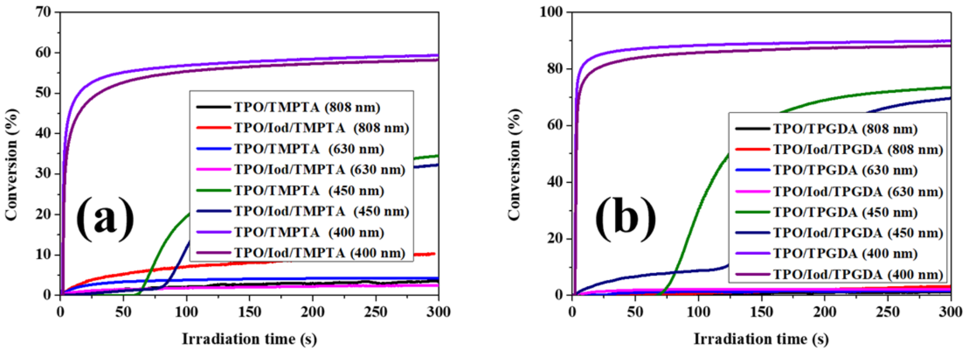

Fig. S13 Photopolymerization kinetics of (a) TPO/TMPTA (0.01:1, mole ratio), TPO/Iod/TMPTA systems (0.01:0.01:1, mole ratio), (b) TPO/TPGDA (0.01:1, mole ratio) and TPO/Iod/TPGDA systems (0.01:0.01:1, mole ratio) upon irradiation at 808 nm laser, 630 nm LED, 450 nm LED and 400 nm UV-LED.

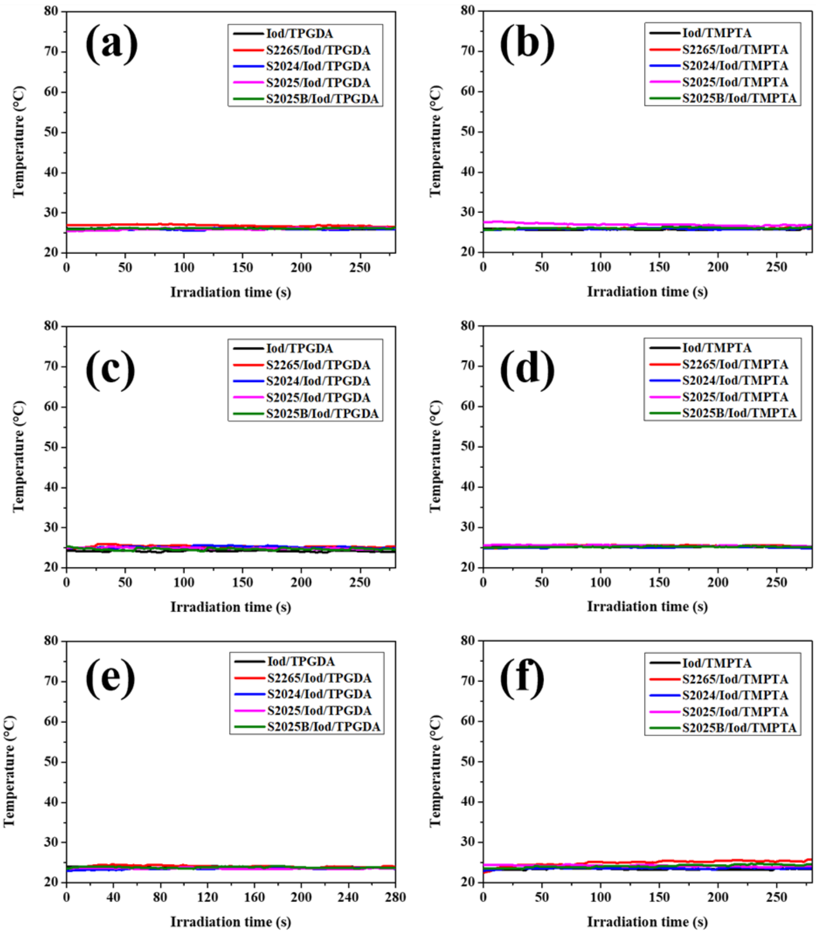

Fig. S14 Curves of temperature maximum versus time recorded by thermal imaging camera in the presence of (a) cyanine/Iod/TPGDA systems under irradiation at 630 nm LED, (b) cyanine/Iod/TMPTA systems under irradiation at 630 nm LED, (c) cyanine/Iod/TPGDA systems under irradiation at 450 nm LED, (d) cyanine/Iod/TMPTA systems under irradiation at 450 nm LED, (e) cyanine/Iod/TPGDA systems under irradiation at 400 nm UV-LED and (f) cyanine/Iod/TMPTA systems under irradiation at 400 nm UV-LED.

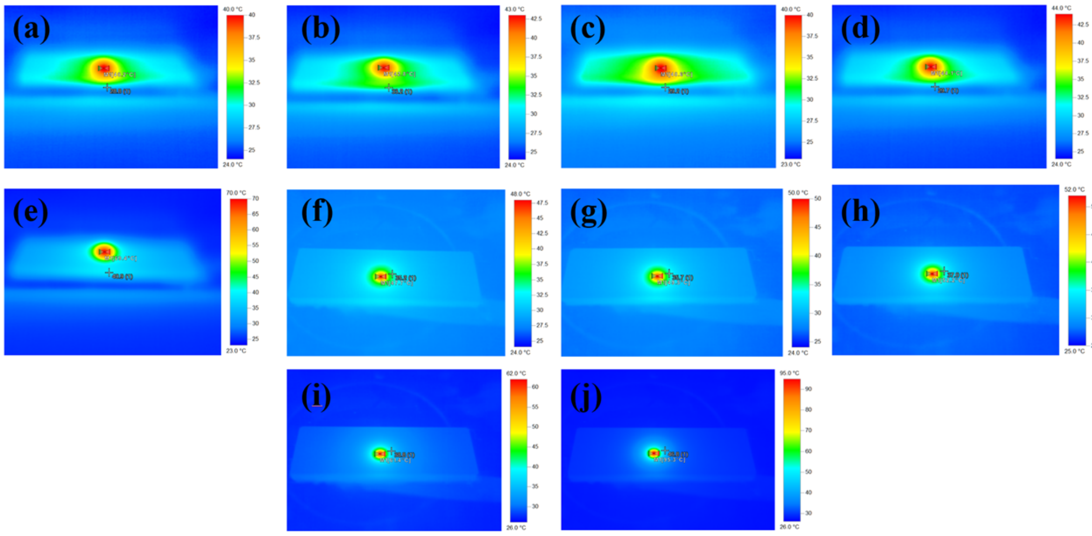

Fig. S15 thermal imaging pictures after irradiation at 808 nm laser, (a) Iod/TPGDA, (b) S2265/Iod/TPGDA, (c) S2024/Iod/TPGDA, (d) S2025/Iod/TPGDA, (e) S2025B/Iod/TPGDA, (f) /Iod/TMPTA, (g) S2265/Iod/TMPTA, (h) S2024/Iod/ TMPTA, (i) S2025/Iod/ TMPTA and (j) S2025B/Iod/ TMPTA.

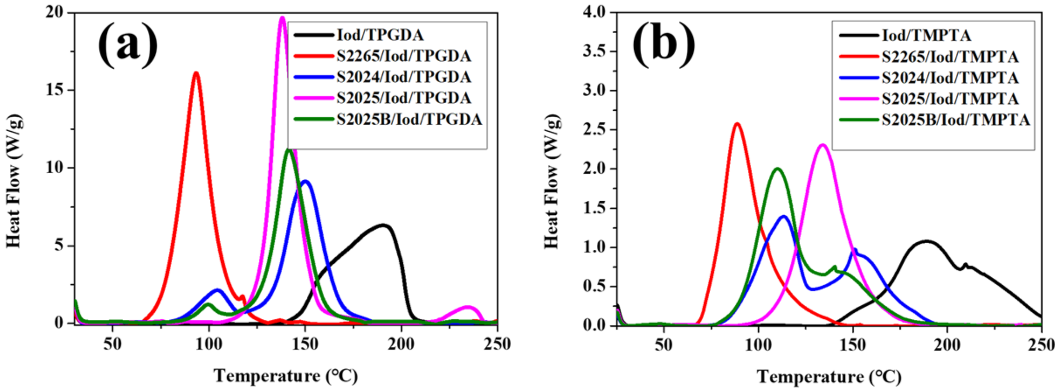

Fig. S16 DSC curves of cyanine/Iod/TPGDA systems (0.002:0.01:1, mole ratio) and cyanine/Iod/TMPTA systems (0.002:0.01:1, mole ratio).

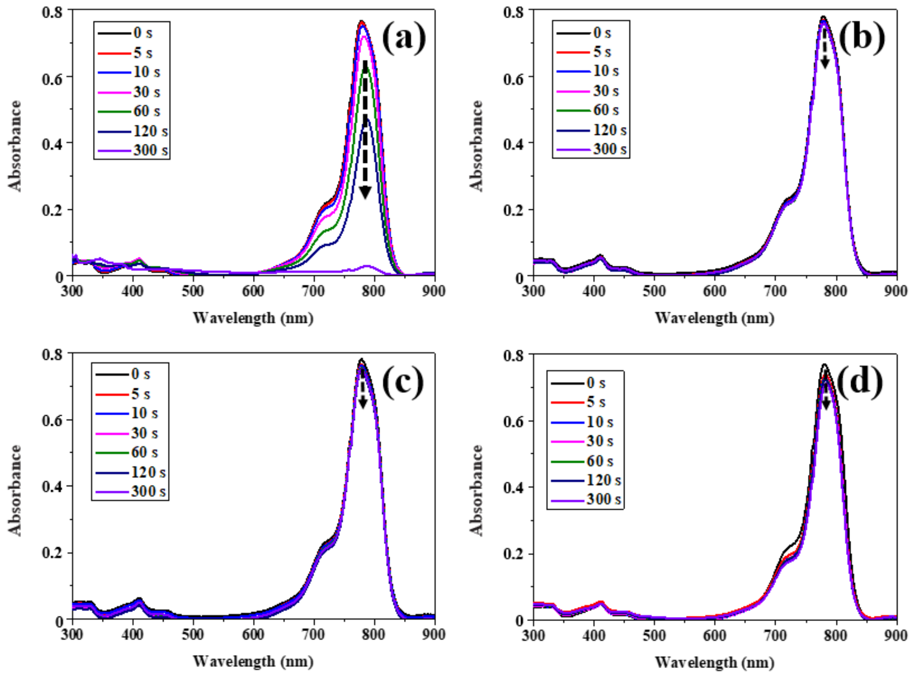

Fig. S17 Photolysis curves of S2265 in anhydrous dichloromethane upon irradiation at (a) 808 nm laser, (b) 630 nm LED, (c) 450 nm LED and (d) 400 nm UV-LED (concentration = 2.0 × 10^{-6} mol L^{-1} for S2265).

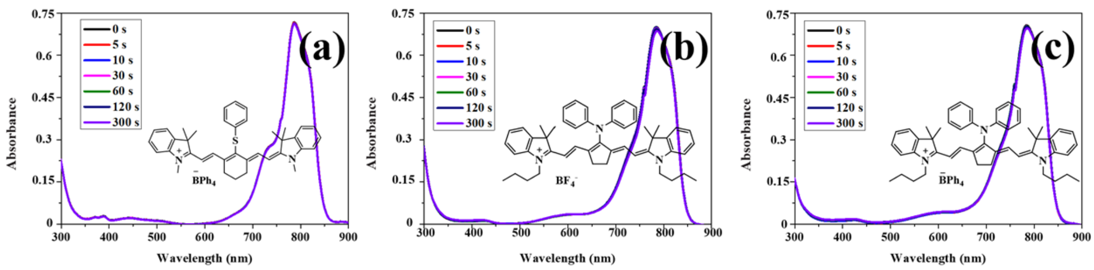

Fig. S18 Photolysis curves of (a) S2024/Iod system, (b) S2025/Iod system and (c) S2025B/Iod system in anhydrous dichloromethane upon irradiation at 630 nm LED (concentration = 2.0 × 10^{-6} mol L^{-1} for cyanines and 8×10^{-6} mol L^{-1} for Iod).

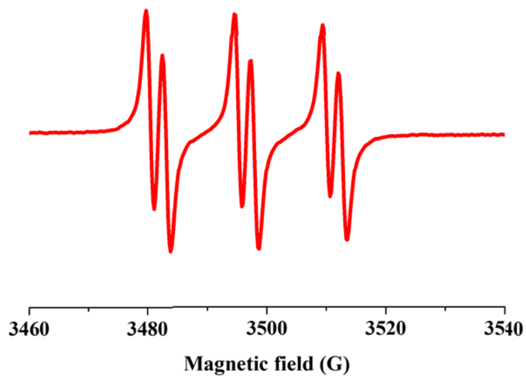

Fig. S19 ESR spectra of Iod under exposure to high-pressure mercury lamp trapped by PBN.

Table S1 Molar extinction coefficients (ε) of cyanines in anhydrous dichloromethane at 808 nm, 630 nm, 450 nm, 400 nm and λ_{max}

cyanines	λ_{max} (nm)	ε (M^{-1} cm^{-1})				
		ε_{max}	ε_{808}	ε_{630}	ε_{450}	ε_{400}
S2265	788	355, 900	171, 200	6, 450	5, 240	11, 500
S2024	803	334, 300	316, 900	2, 640	4, 350	2, 980
S2025	802	255, 000	243, 300	7, 160	920	1, 860
S2025B	802	262, 300	250, 500	7, 290	860	1, 880

Table S2 Final double bond conversion of cyanine/Iod/TMPTA systems under irradiation at 808 nm laser, 630 nm LED, 450 nm LED and 400 nm UV-LED

	Final conversion (%)			
	808 nm	630 nm	450 nm	400 nm
Iod	11.2	2.0	5.8	8.4
S2265/Iod	43.7	40.0	51.7	42.3
S2024/Iod	47.2	13.4	52.8	42.9
S2025/Iod	49.0	11.2	29.5	34.5
S2025B/Iod	63.3	30.8	47.0	49.9

Table S3 Final double bond conversion of cyanine/Iod/TPGDA systems under irradiation at 808 nm laser, 630 nm LED, 450 nm LED and 400 nm UV-LED

	Final conversion (%)			
	808 nm	630 nm	450 nm	400 nm
Iod	2.4	2.4	1.6	2.9
S2265/Iod	73.8	77.5	67.8	73.1
S2024/Iod	79.3	0.3	71.6	84.7
S2025/Iod	77.2	0.6	4.21	49.0
S2025B/Iod	89.5	3.3	56.3	80.3

Table S4 Parameters Characterizing the Reactivity of cyanines with Iod

	E_{ox} (V)	E_{red} (V)	ΔG (eV)
S2265	0.480[a]	-0.970[a]	-0.454
S2024	0.588	-0.620	-0.316
S2025	0.515	-0.686	-0.391
S2025B	0.521	-0.681	-0.385
Iod		-0.640[a]	

[a] Datas were quoted from reference [1].

REFERENCES

1. Strehmel, B.; Schmitz, C.; Kutahya, C.; Pang, Y.; Drewitz, A.; Mustroph, H., Photophysics and photochemistry of NIR absorbers derived from cyaniness: key to new technologies based on chemistry 4.0. *Beilstein J Org Chem* **2020,** *16*, 415-444.