Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and free radical photopolymerization of triphenylamine-based oxime ester photoinitiators

Zhong-Han Lee[a], Fatima Hammoud[b,c,d], Akram Hijazi[d], Bernadette Graff[b,c], Jacques Lalevée[b,c*], Yung-Chung Chen[a,e*]

[a.] Department of Chemical and Materials Engineering, National Kaohsiung University of Science and Technology, Kaohsiung 80778, Taiwan

[b.] Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100, Mulhouse, France

[c.] Université de Strasbourg, France

[d.] EDST, Université Libanaise, Campus Hariri, Hadath, Beyrouth, Liban

[e.] Photo-SMART (Photo-sensitive Material Advanced Research and Technology Center), National Kaohsiung University of Science and Technology, Kaohsiung City 80778, Taiwan

*Corresponding authors: Y. C. Chen (chenyc@nkust.edu.tw)

JacquesLalevée (jacques.lalevee@uha.fr)

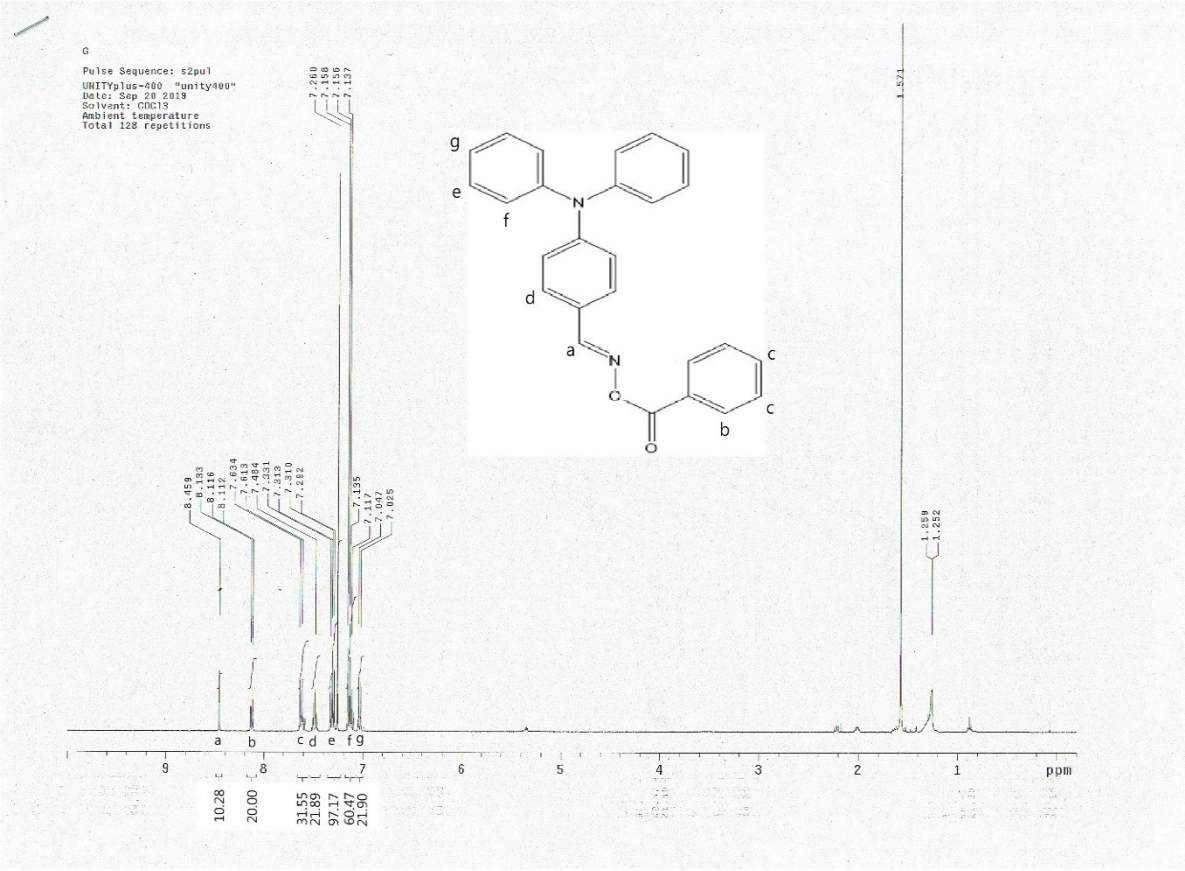


Fig. S1 ^{1}H NMR of the **TP-1**.

Fig. S2 ^{1}H NMR of the **TP-2**.

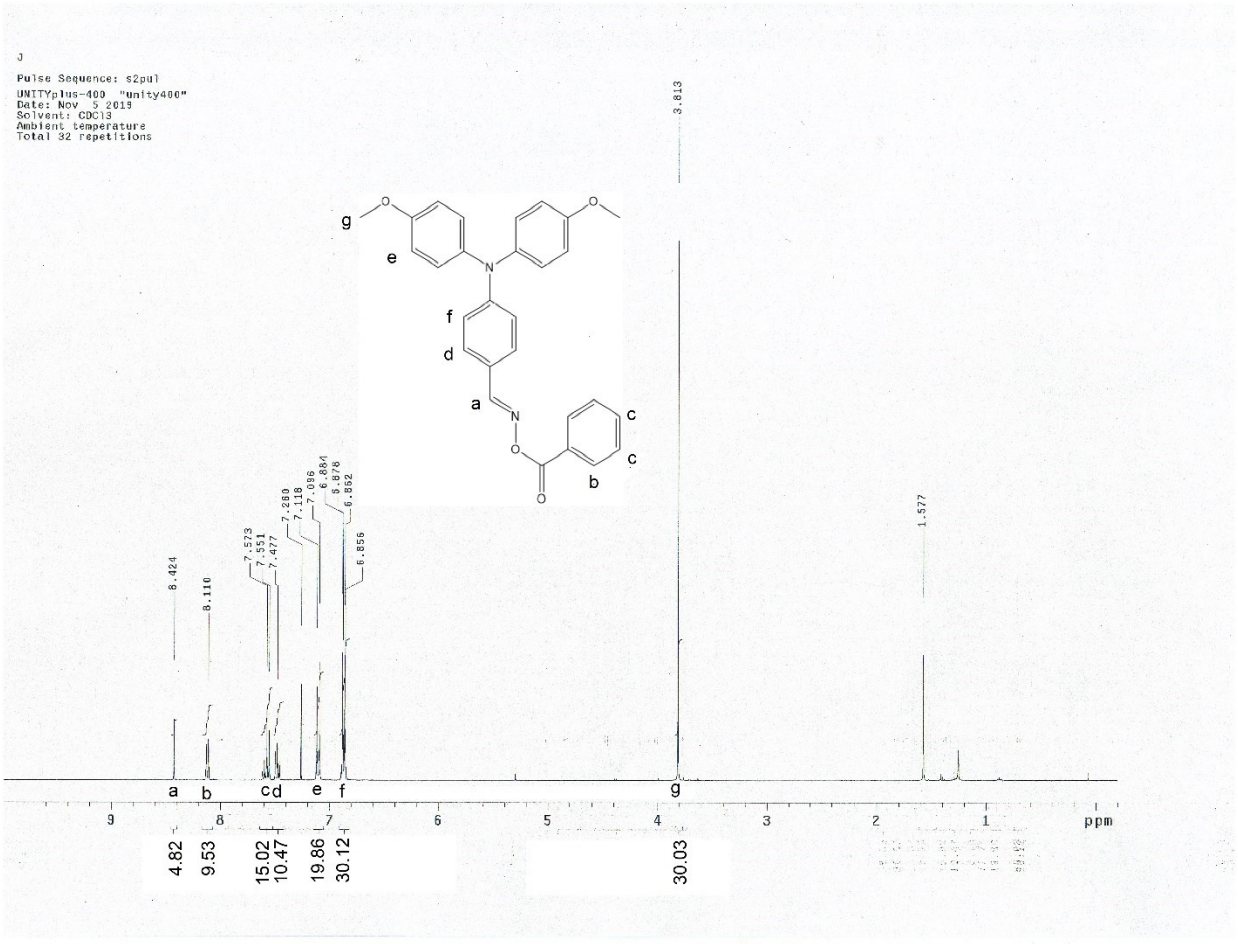


Fig. S3 ^{1}H NMR of the **TP-3**.

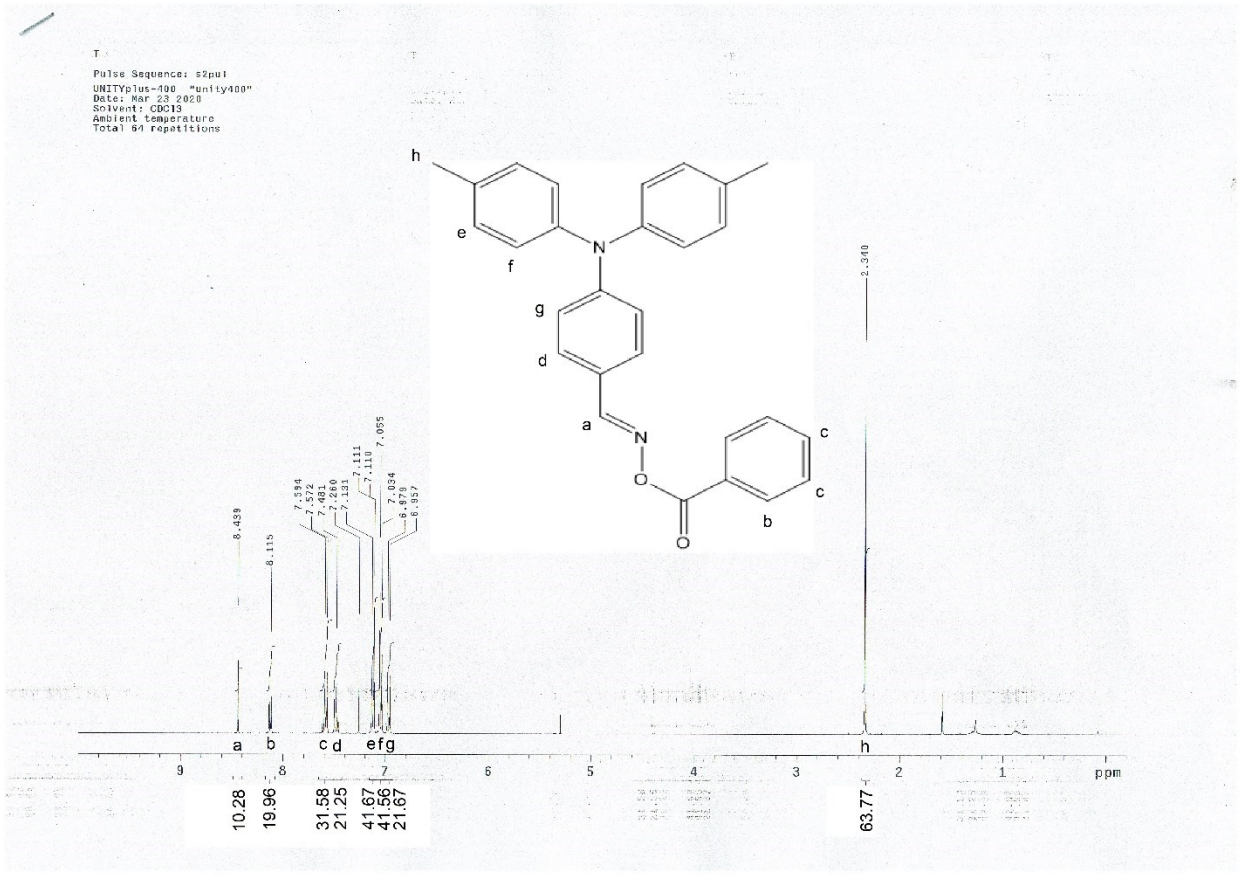


Fig. S4 ^{1}H NMR of the **TP-4**.

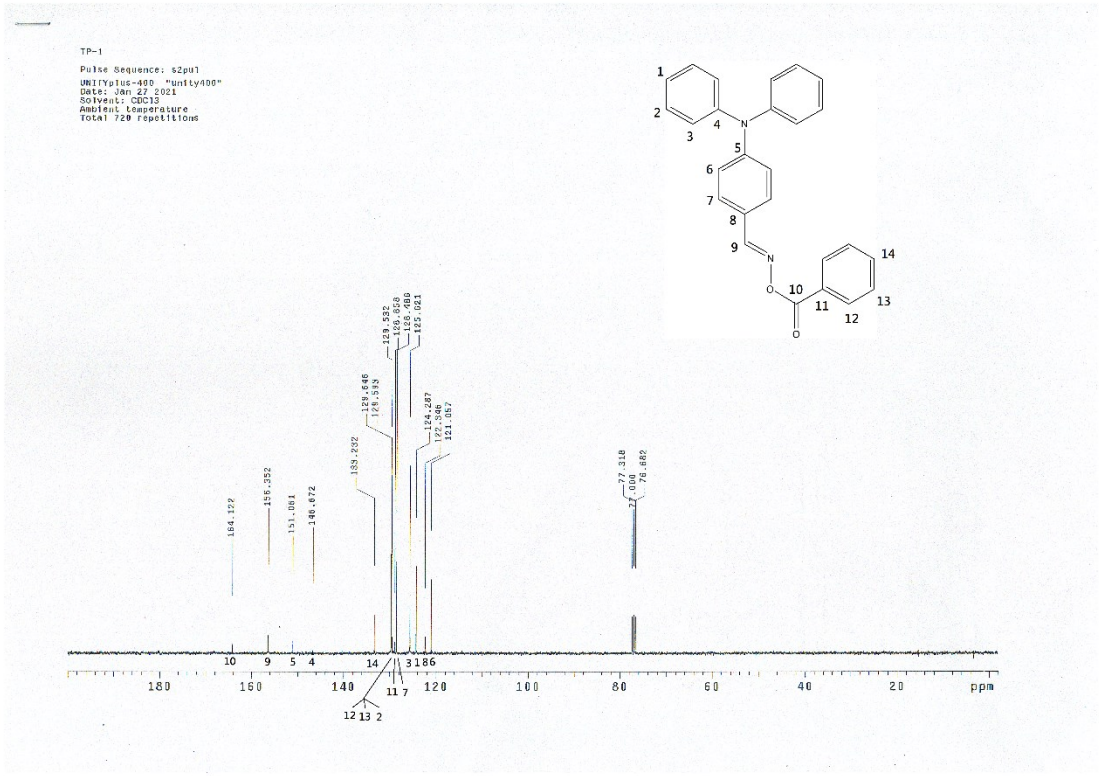


Fig. S5 ^{13}C NMR of the **TP-1**.

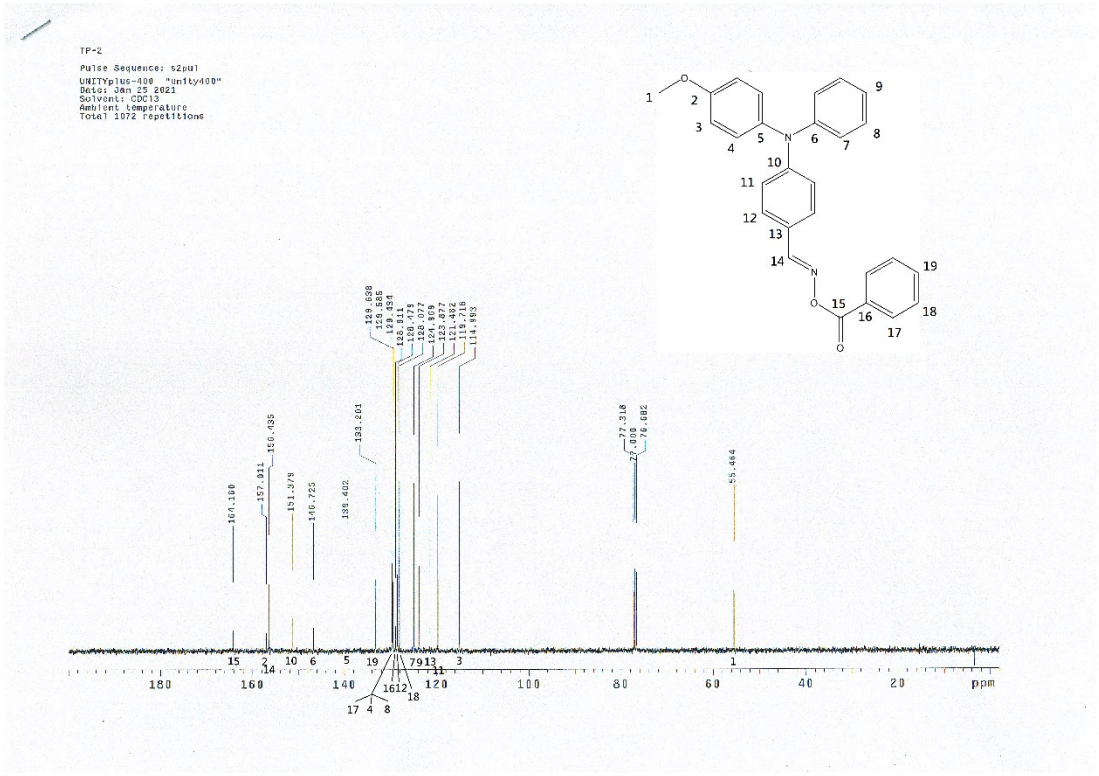


Fig. S6 ^{13}C NMR of the **TP-2**.

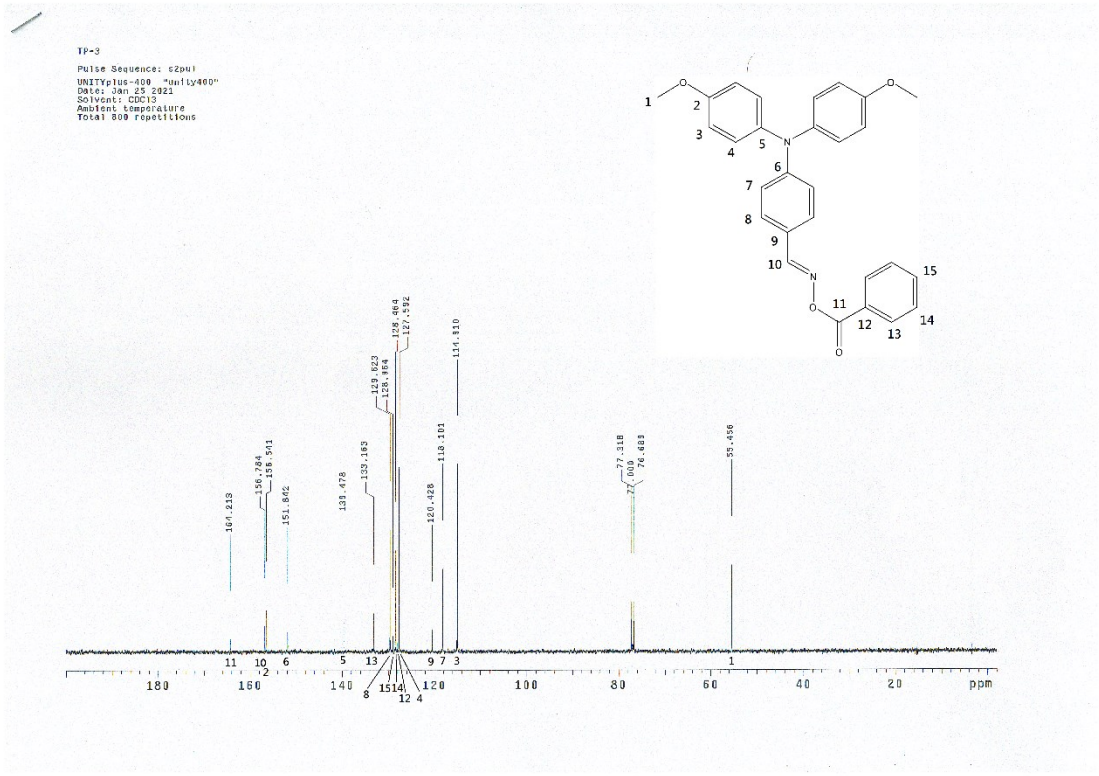


Fig. S7 ^{13}C NMR of the **TP-3**.

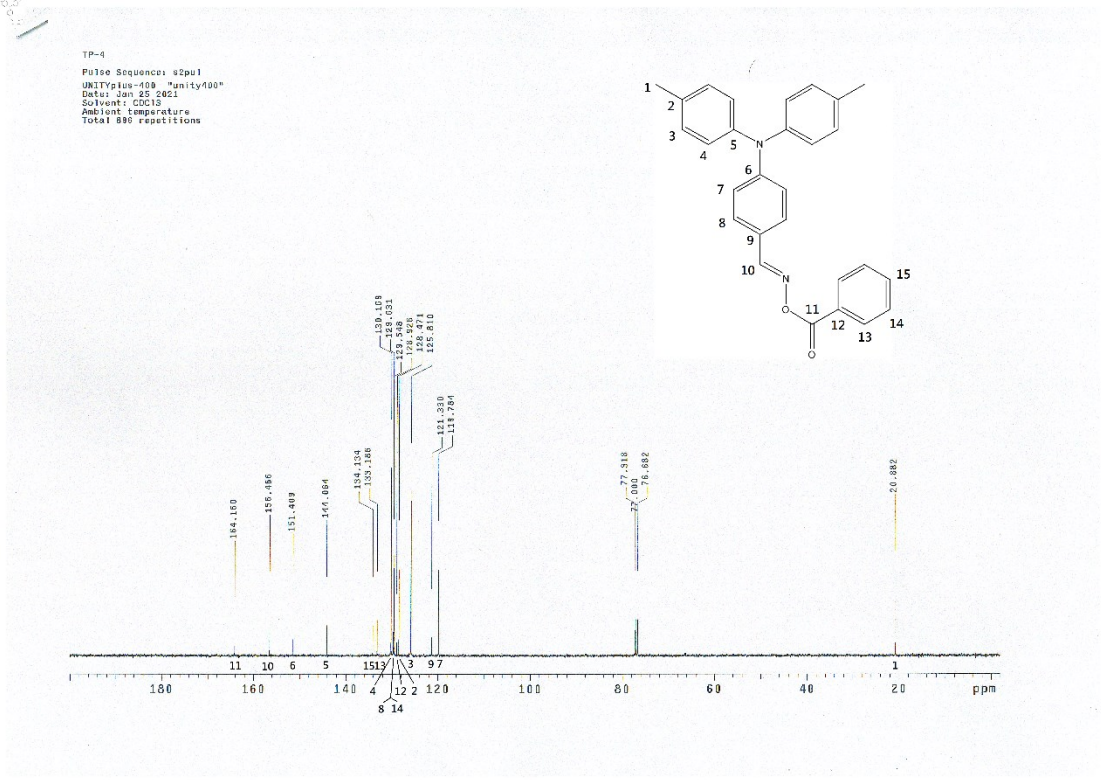
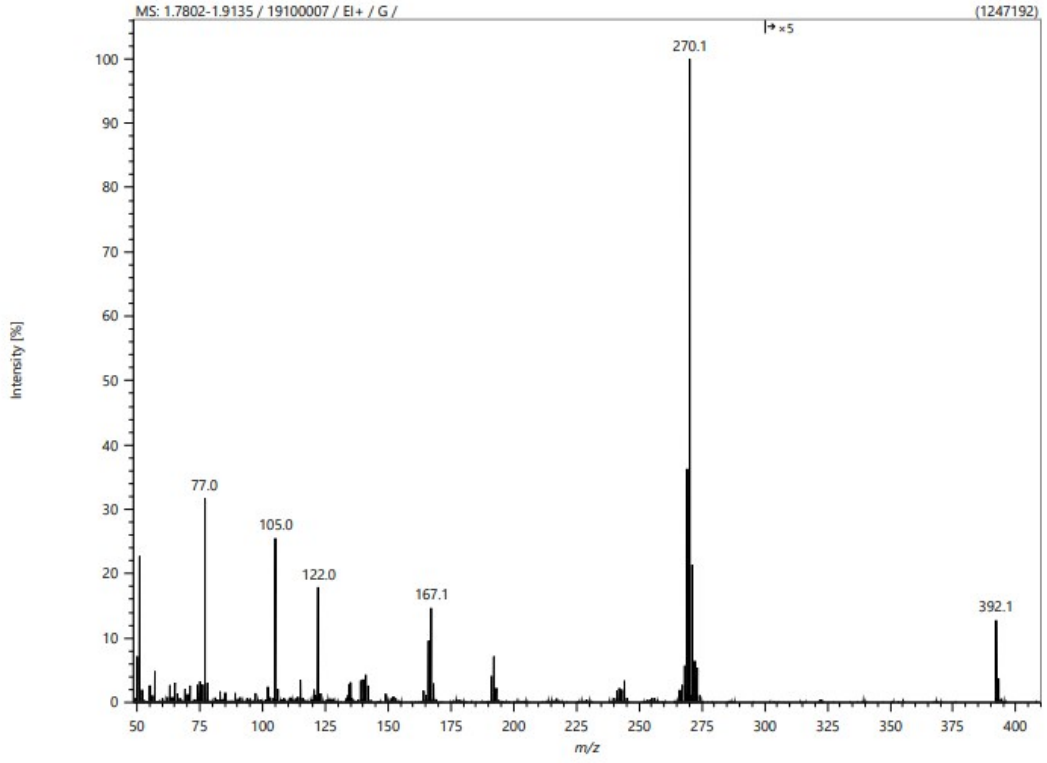
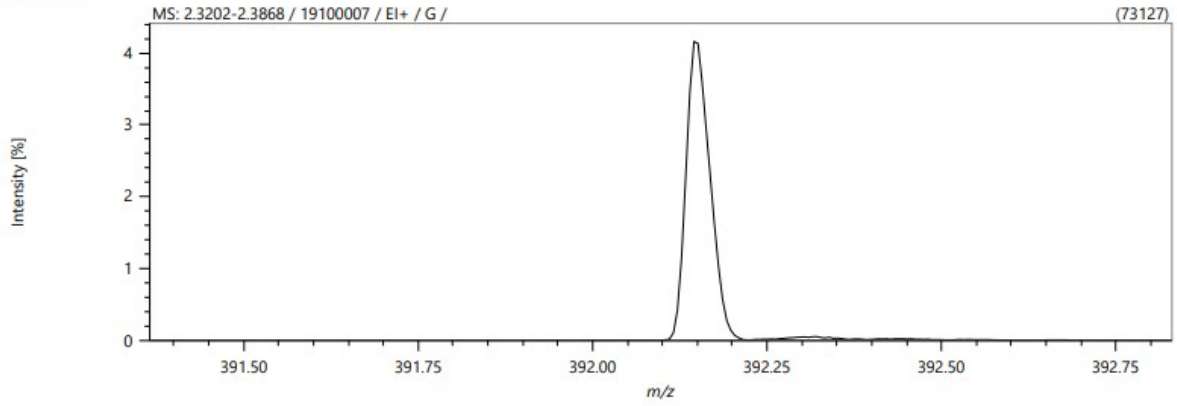


Fig. S8 ^{13}C NMR of the **TP-4**.



Spectrum



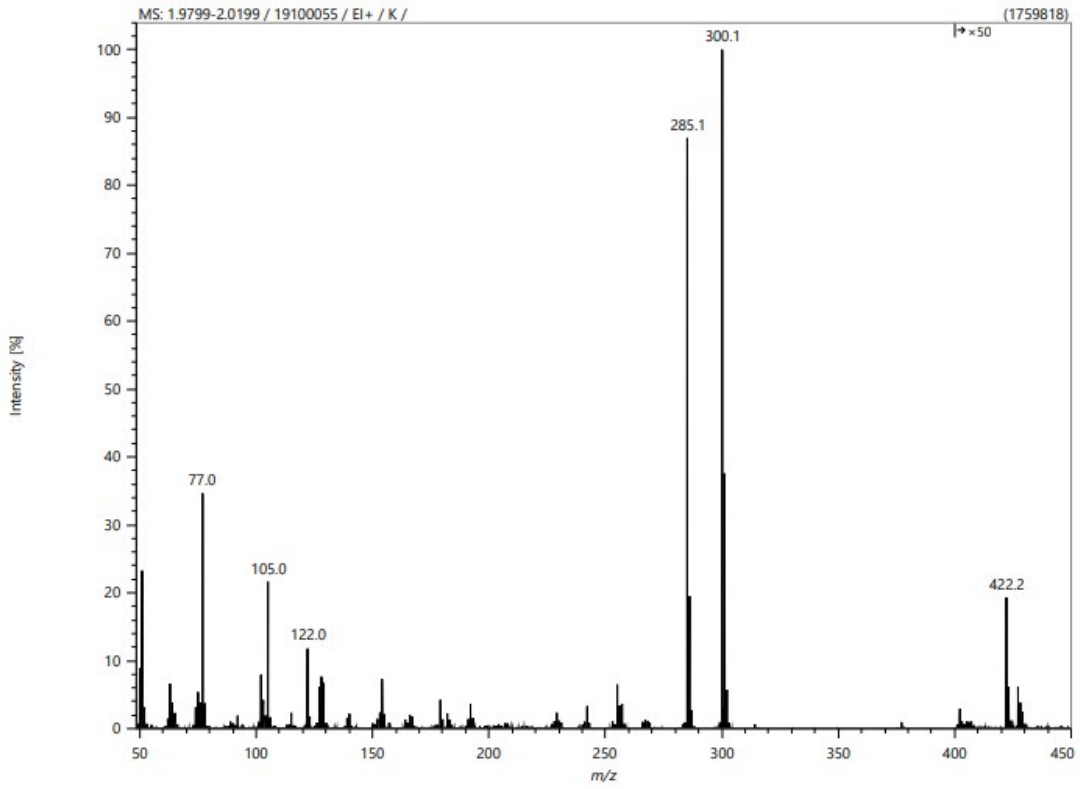
Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 ppm	Symbol	C	H	S	F	N	O	P
Electron:	Odd/Even	Min	0	0	0	0	0	0	0
Charge:	+1	Max	26	20	0	0	2	4	1
DBE:	-1.5 - 200.0								

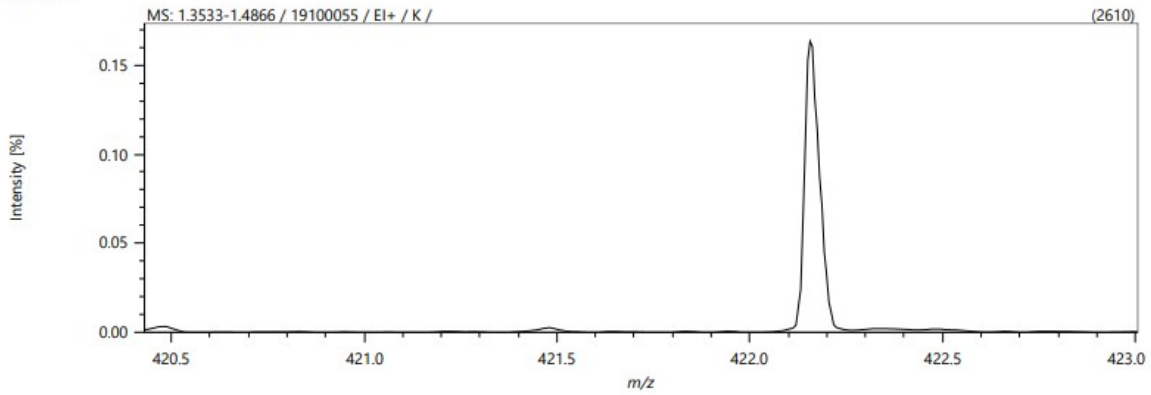
Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
392.15178	73127.44	C26 H20 N2 O2	392.15193	-0.15	-0.37	18.0

Fig. S9 Electron impact mass spectrometry (EI-MS) of the **TP-1**.



Spectrum



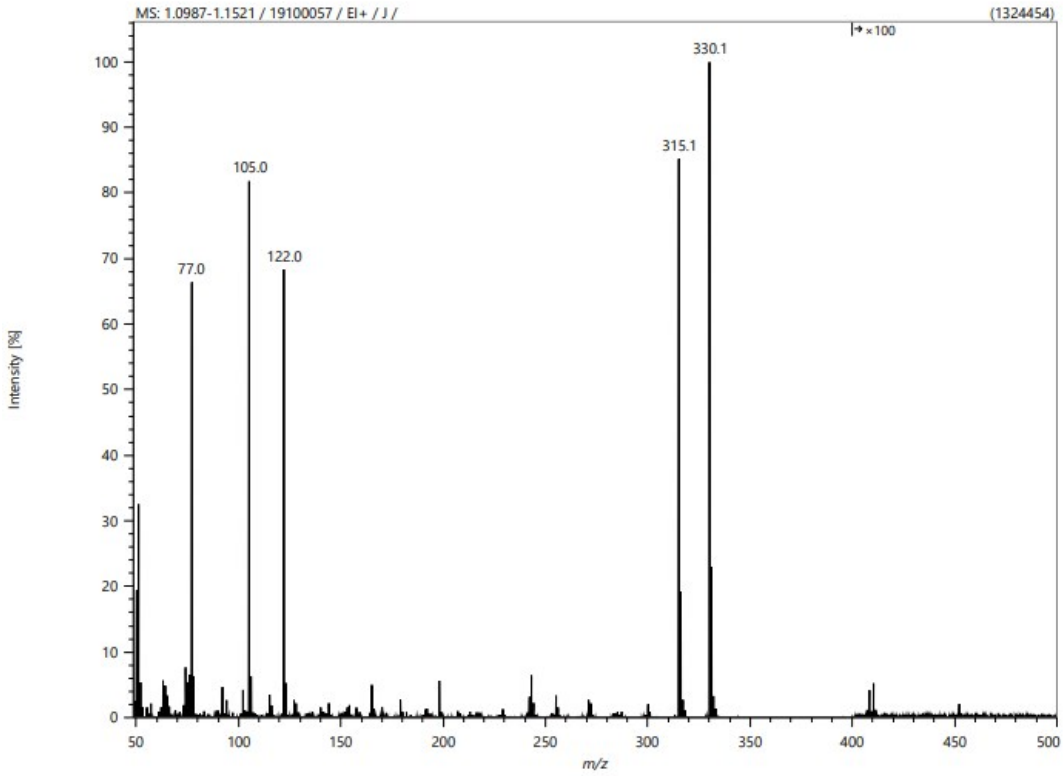
Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 ppm	Symbol	C	H	Br	P	N	O	Si
Electron:	Odd/Even	Min	0	0	0	0	0	0	0
Charge:	+1	Max	27	22	0	0	2	3	1
DBE:	-1.5 - 200.0								

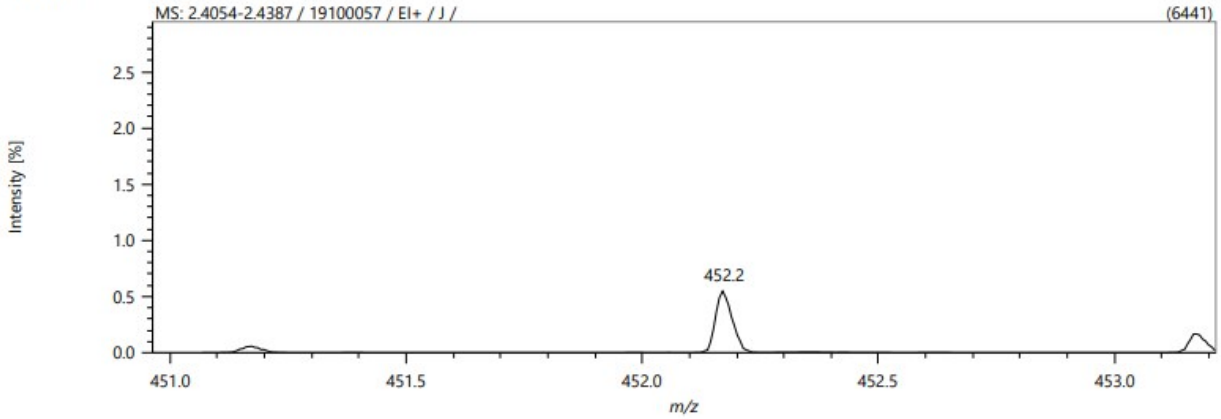
Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
422.16226	2609.85	C27 H22 N2 O3	422.16249	-0.24	-0.56	18.0

Fig. S10 Electron impact mass spectrometry (EI-MS) of the **TP-2**.



Spectrum



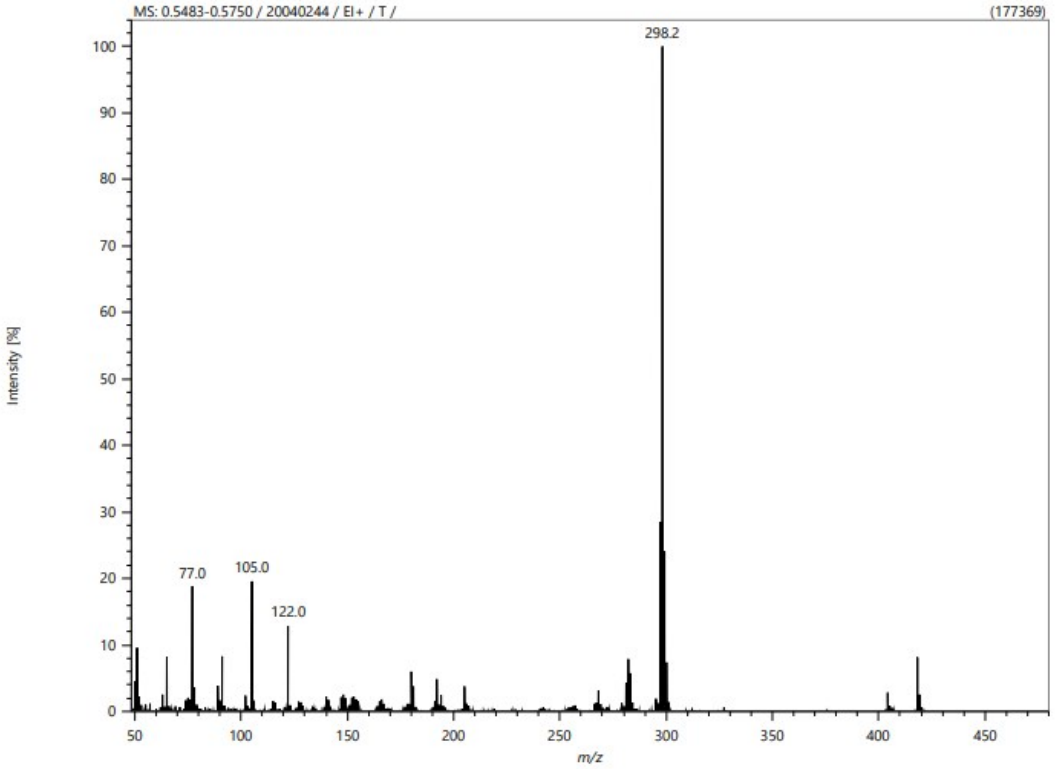
Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 ppm	Symbol	C	H	Br	P	N	O	Si
Electron:	Odd/Even	Min	0	0	0	0	0	0	0
Charge:	+1	Max	28	24	0	0	2	4	1
DBE:	-1.5 - 200.0								

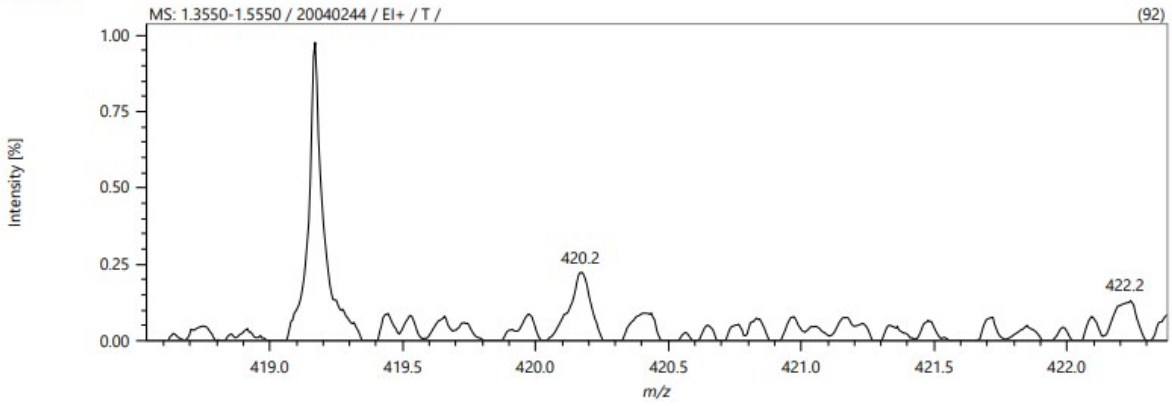
Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
452.17329	6440.96	C28 H24 N2 O4	452.17306	0.23	0.51	18.0

Fig. S11 Electron impact mass spectrometry (EI-MS) of the **TP-3**.



Spectrum



Elemental Composition

Parameters	
Tolerance:	±5.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-1.5 - 200.0

Elements Set 1:

Symbol	C	H	S	Si	N	O	Cl
Min	0	0	0	0	0	0	0
Max	28	24	2	0	2	2	0

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
420.16526	21.04	C28 H24 N2 S	420.16547	-0.21	-0.50	18.0

Fig. S12 Electron impact mass spectrometry (EI-MS) of the **TP-4**.

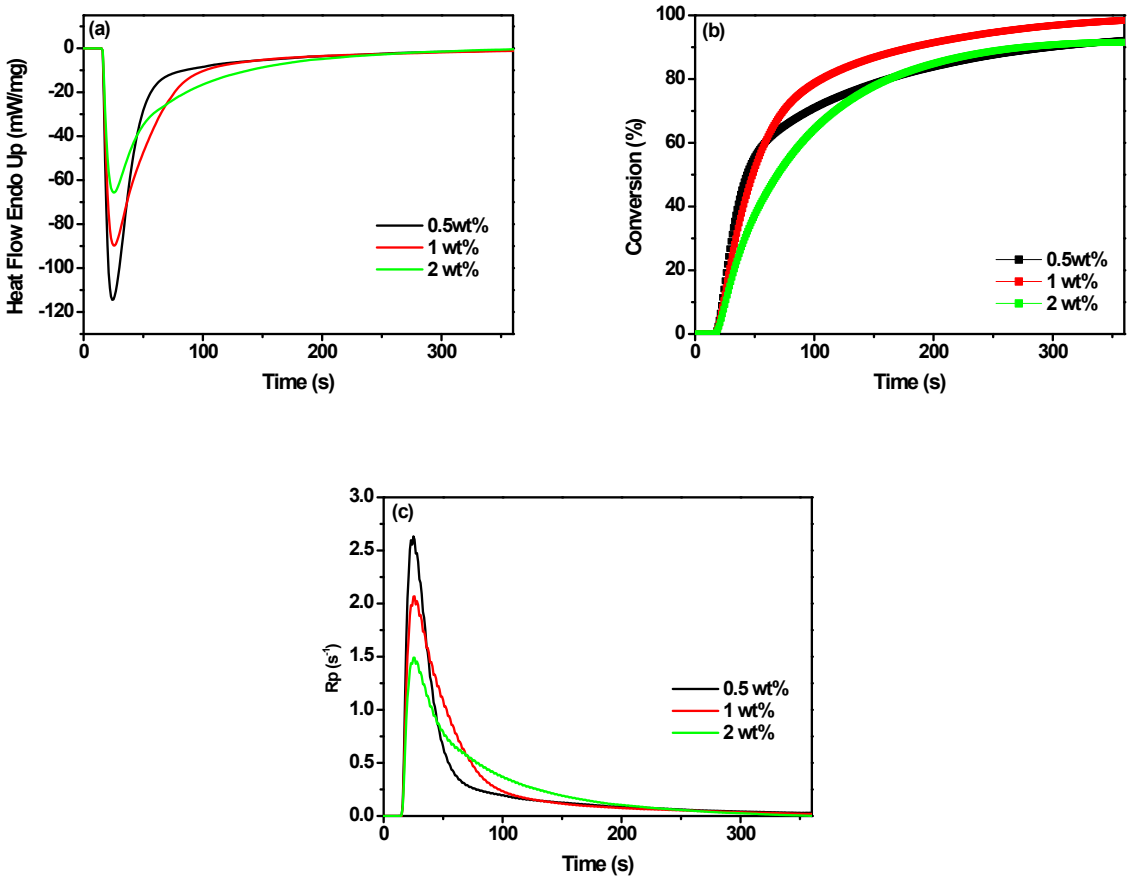


Fig. S13 (a) Heat flow versus time, (b) conversion versus time and (c) Rp versus time of TMPTA photopolymerization initiated by various weight ratios of **TP-1** (0.5, 1 wt% and 2 wt%) under UV light irradiation. The irradiation starts for t = 24 s.

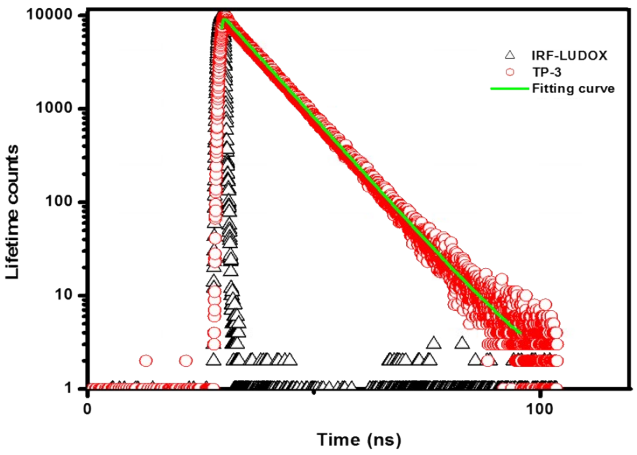


Fig. S14 Time correlated single photon counting of **TP-3** in CH_2Cl_2, λ_{ex}= 367 nm, λ_{em}= 550 nm, mono-exponential curve fitting.

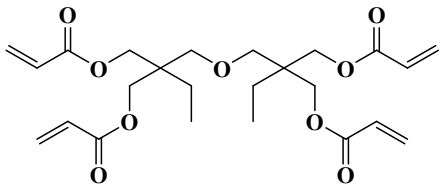


Fig. S15 Structure of the ditrimethylolpropane tetraacrylate (TA) monomer.

Table S1 Photo-DSC results derived from various weight ratios of **TP-1** (0.5, 1 wt% and 2 wt%)[a]

TP-1 (wt%)	Final Conversion (%)	ΔHt (kJ/mol)[b]	H_{max} (mW/mg)[c]	Rp_{max} (s^{-1})[d]	T_{max} (s)[e]
0.5	94	81	114	2.63	24
1	99	85	90	2.07	26
2	92	79	66	1.49	25

[a.] Measured with 180 mW cm^{-2} of UV light (λ: 250-450 nm) for 6 min.
[b.] .ΔHt is the totally reaction heat enthalpy within 6 min.
[c.] H_{max}: maximum heat flow values.
[d.] Rp_{max}: maximum rate of polymerization.
[e.] T_{max}: time at maximum heat flow.

Table S2 Fluorescence lifetime of **TP-1–4** in CH_2Cl_2.

First singlet state lifetime (ns)			
TP-1	**TP-2**	**TP-3**	**TP-4**
0.85	0.8	8	1.6