Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Novel applications of fluorescent brighteners in aqueous visible-light photopolymerizations: high performance water-based coating and LED-assisted hydrogel synthesis

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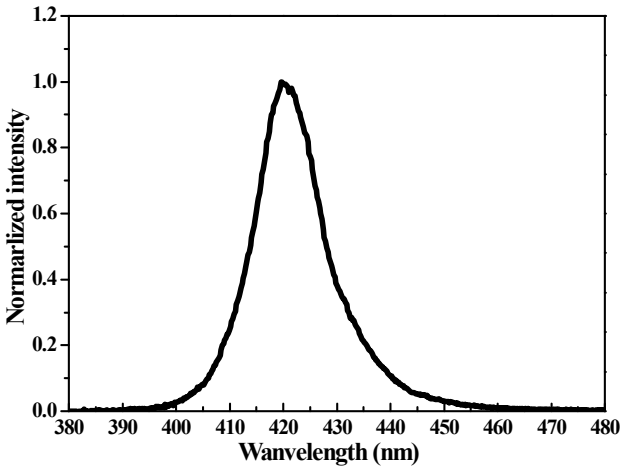


Figure S1 Emission spectrum of the irradiation source LED@420 nm (M420-L3, Thorlabs, ~ 40 mW cm^{-2}).

Table S1 Photopolymerization data of the Ebecryl 605/water blends with different water concentration obtained under air and exposure to LED@420 nm in the presence of various brighteners-based PISs.

PISs	Ebecryl 605 (100 wt%)		Ebecryl 605/water (90%/10%, w/w)		Ebecryl 605/water (80%/20%, w/w)		Ebecryl 605/water (70%/30%, w/w)	
	FC (%)	PR($R_p/[M_0]$* 100)	FC (%)	PR($R_p/[M_0]$* 100)	FC (%)	PR($R_p/[M_0]$* 100)	FC (%)	PR($R_p/[M_0]$* 100)
TFB/IOD (0.5%/1%, w/w)	47.3 ± 1.2%	0.74 ± 0.1	58.7 ± 1.8%	1.74 ± 0.2	61.5 ± 2.0%	4.26 ± 0.05	43.1 ± 2.1%	0.67 ± 0.2
C1/IOD (0.1%/1%, w/w)	40.9 ± 2.2%	0.54 ± 0.2	42.2 ± 2.8%	0.84 ± 0.07	50.2 ± 1.7%	0.60 ± 0.1	42.1 ± 1.9%	0.65 ± 0.1
CBUS 450/IOD (2%/2%, w/w)	30.2 ± 1.9%	0.52 ± 0.1	63.1 ± 2.1%	1.45 ± 0.08	52.9 ± 1.5%	1.41 ± 0.2	49.8 ± 0.7%	1.24 ± 0.2
CBS X/IOD (0.1%/1%, w/w)	38.5 ± 2.9%	1.13 ± 0.06	45.4 ± 2.6%	1.10 ± 0.15	50.6 ± 1.9%	1.68 ± 0.2	45.2 ± 1.3%	1.16 ± 0.13
BBT/IOD (1%/2%, w/w)	37.1 ± 1.8%	0.59 ± 0.3	49.4 ± 2.7%	0.84 ± 0.1	42.1 ± 2.2%	0.68 ± 0.3	39.1 ± 1.5%	0.53 ± 0.3

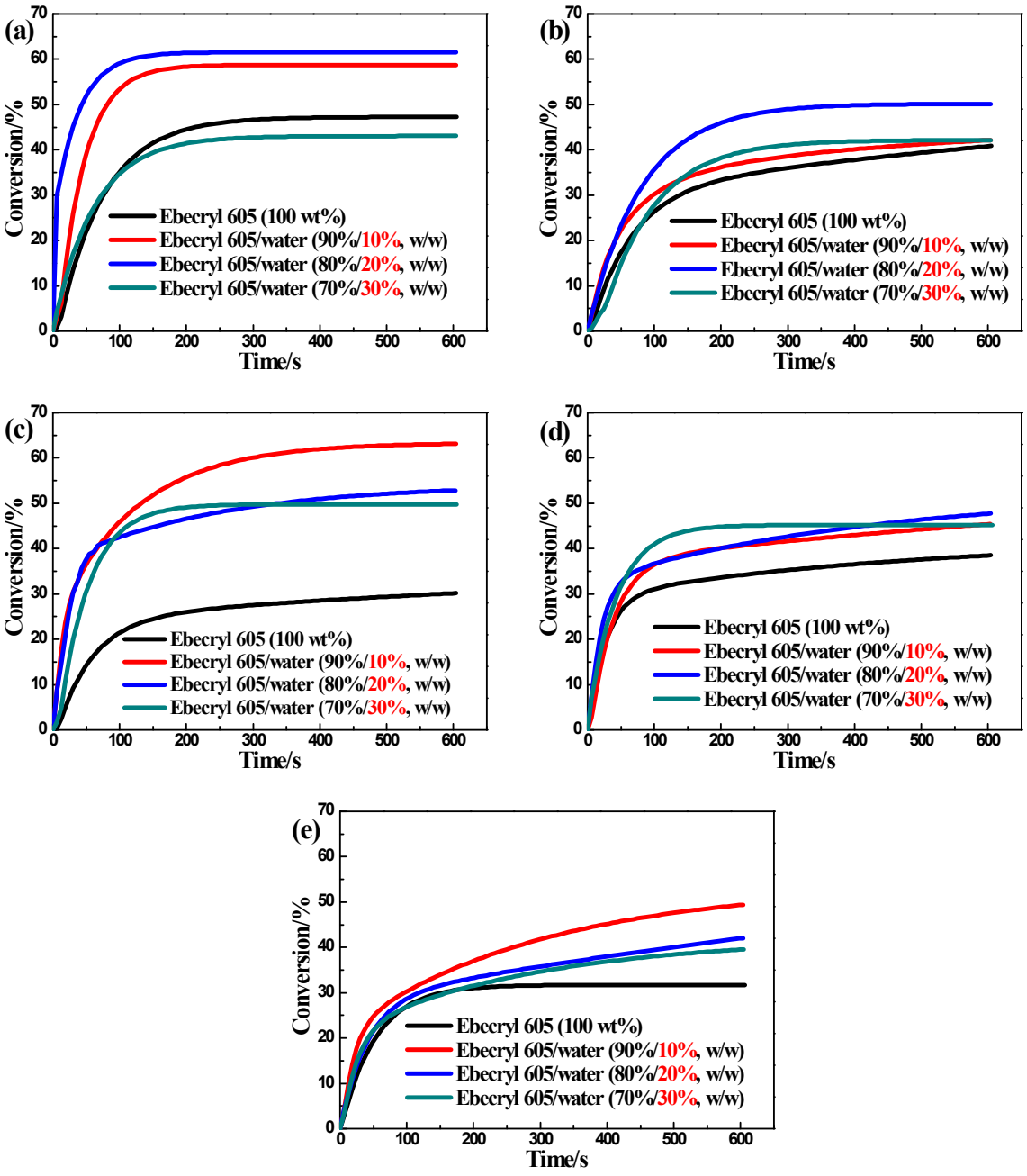


Figure S2 Photopolymerization profiles (acrylate function conversion *vs*. time) of Ebecryl 605/water blends with different water contents under air in the presence of (a) TFB/IOD (0.5%/1%, w/w) (b) C 1/IOD (0.1%/1%, w/w) (c) CBUS 450/IOD (2%/2%, w/w) (d) CBS X/IOD (0.1%/1%, w/w) (e) BBT/IOD (1%/2%, w/w) PISs upon LED@420 nm exposure.

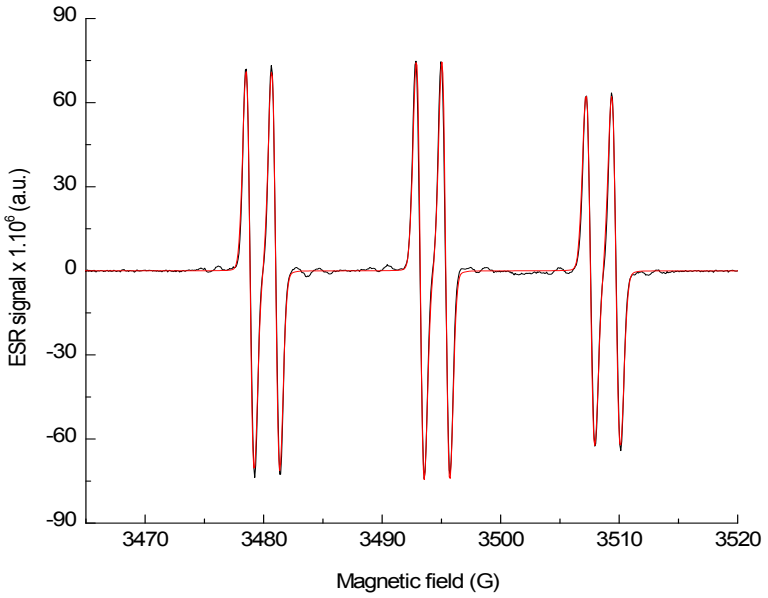


Figure S3 ESR-ST spectrum of the CBUS 450/IOD system in tert-butylbenzene nitrogen saturated solution after light irradiation at 385 nm. Experimental (-----), simulated (-----).

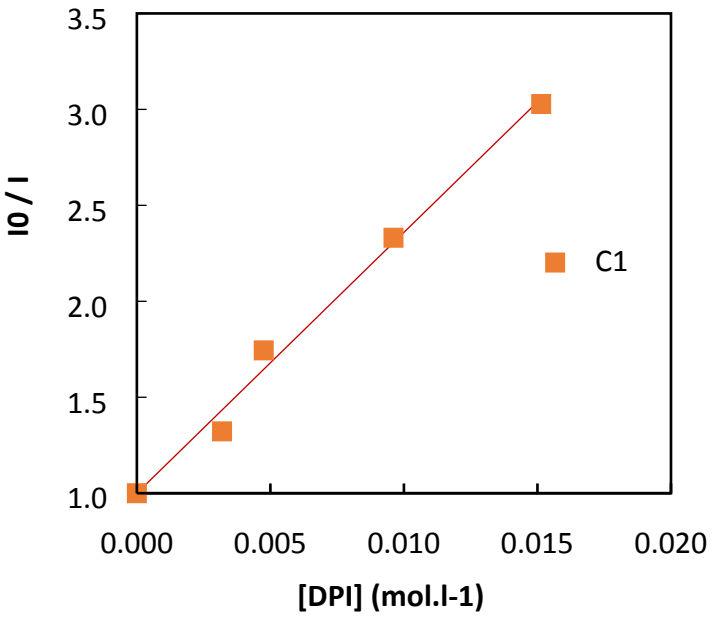


Figure S4 Stern-Volmer plot for the steady state fluorescence quenching.

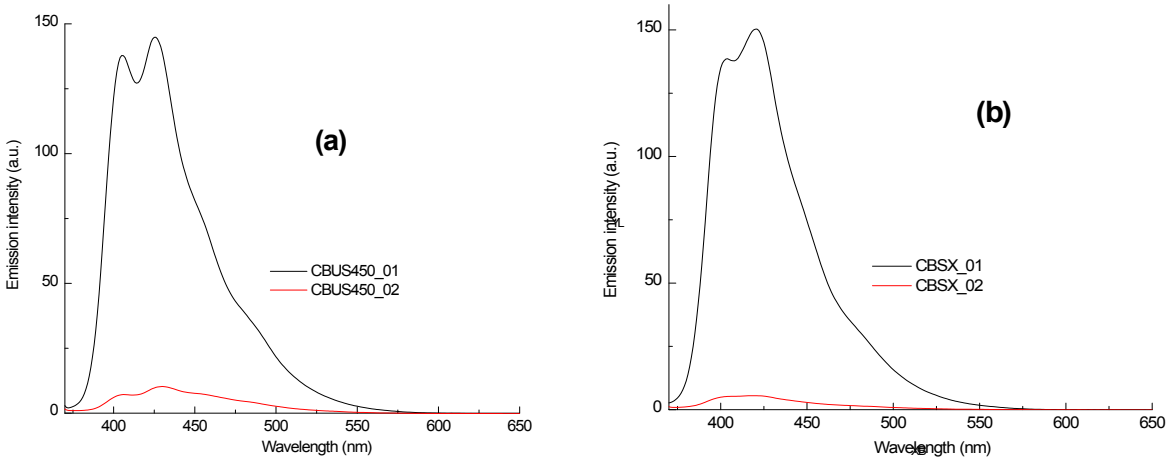


Figure S5 Steady state fluorescence quenching experiments for a) CBUS450 in absence (----) and in presence (----) of IOD ([IOD] = 1.0 mM), b) CBSX in absence (----) and in presence (----) of IOD ([IOD] = 4.3 mM).

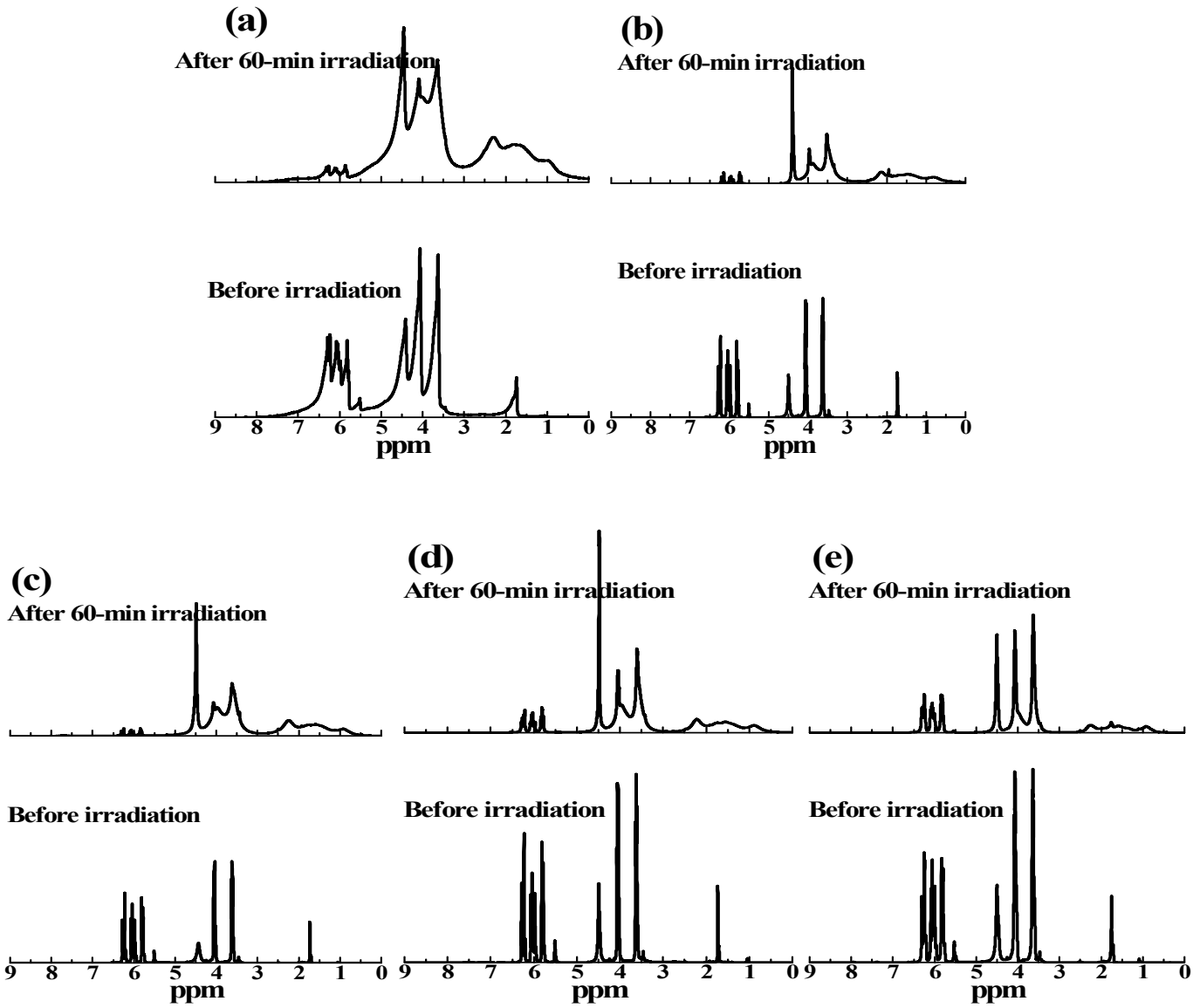
Table S2. Hyperfine coupling constants gathered through ESR-ST experiments. LED irradiation centers at 385 nm.

Compounds	TFB	BBT	C1 [a]	CBUS 450	CBS X
a_N (G)	14.3	14.3	14.4	14.3	14.3
a_H (G)	2.1	2.1	2.2	2.1	2.1

[a] Key: confidency upon hfc is ± 0.1 G.

Table S3 Final conversion of vinylic bond of HEA in the presence of different PISs obtained from photolysis kinetics varies from 0- to 60-min irradiation and 60-min of LED exposure directly.

Conversion	Before irradiation	After 15-min irradiation	After 30-min irradiation	After 45-min irradiation	After 60-min irradiation	60-min irradiation directly
TFB/IOD	-	63.2%	88.7%	94.4%	97.7%	87.2%
C 1/IOD	-	45.7%	82.9%	95.5%	95.5%	88.9%
CBUS 450/IOD	-	68.1%	90.6%	98.5%	99.6%	93.3%
CBS X/IOD	-	56.8%	77.3%	83.7%	85.8%	72.1%
BBT/IOD	-	3.7%	13.1%	29.1%	44.3%	42.2%


(a)
After 60-min irradiation
Before irradiation
(b)
After 60-min irradiation
Before irradiation
(c)
After 60-min irradiation
Before irradiation
(d)
After 60-min irradiation
Before irradiation
(e)
After 60-min irradiation
Before irradiation
9 8 7 6 5 4 3 2 1 0
ppm

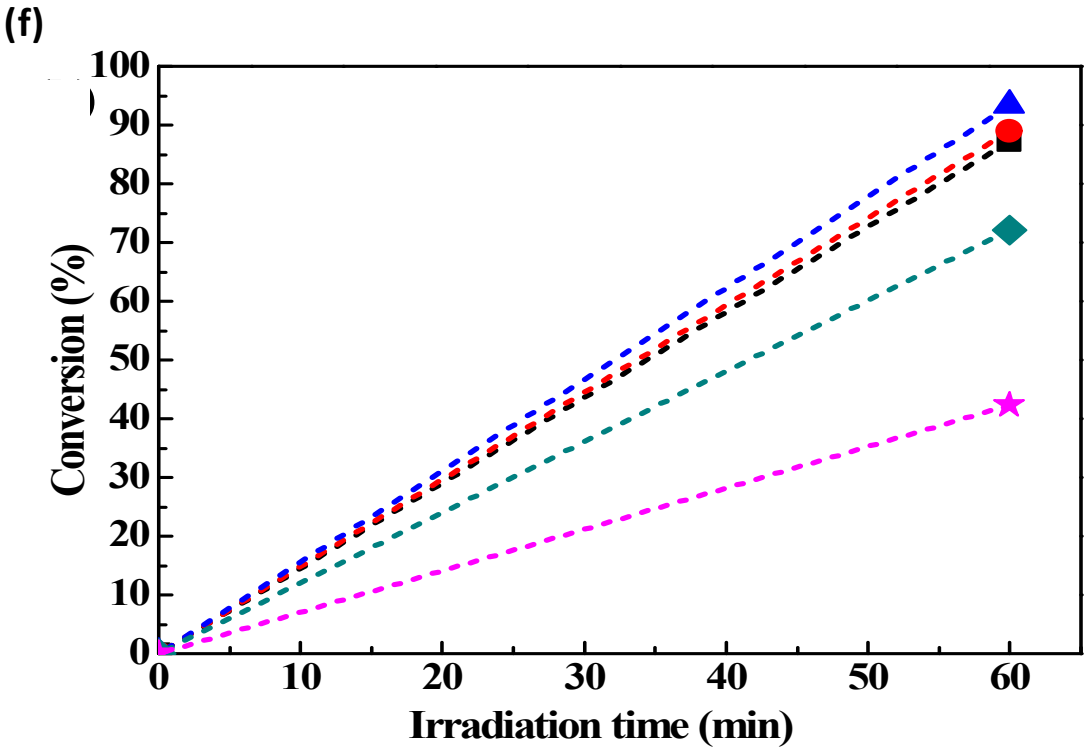


Figure S6 ^{1}H NMR spectra of HEA in a mixed solution (HEA/D_2O/*d*-DMSO blends ([HEA] = 4.4 M; [D_2O] = 25.5 M; [*d*-DMSO] = 1.1 M; the volume ratio of HEA/D_2O = 1:1) after N_2-bubbling before and after 60-min irradiation in the presence of (a) TFB/IOD; (b) C 1/IOD; (c) CBUS 450/IOD; (d) CBS X/IOD PISs; (e) BBT/IOD PISs. (f) Conversion vs. irradiation time. All the tests were carried out at ambient temperature. For all samples, [TFB] = [CBUS 450] = 2.0 mM; [C 1] = 8.0 mM; [CBS X] = 3.3 mM; [BBT] = 4.3 mM; [IOD] = 4.4 mM.

Table S4 Final conversion of vinylic bond of HEA with different volume ratios of HEA/D_2O mixtures without *d*-DMSO in the presence of CBS X/IOD PIS before and after LED exposure.

The volume ratios of HEA/D2O mixtures	Before irradiation	After 15-min irradiation	After 30-min irradiation	After 45-min irradiation	After 60-min irradiation
1/5	-	2.2%	5.9%	7.8%	9.3%
1/2	-	28.1%	37.8%	45.6%	53.3%
1/1	-	53.2%	63.6%	68.8%	69.9%
2/1	-	56.7%	72.4%	78.7%	82.5%
5/1	-	42.5%	53.4%	67.2%	73.5%
11/1	-	40.7%	50.4%	56.4%	64.4%

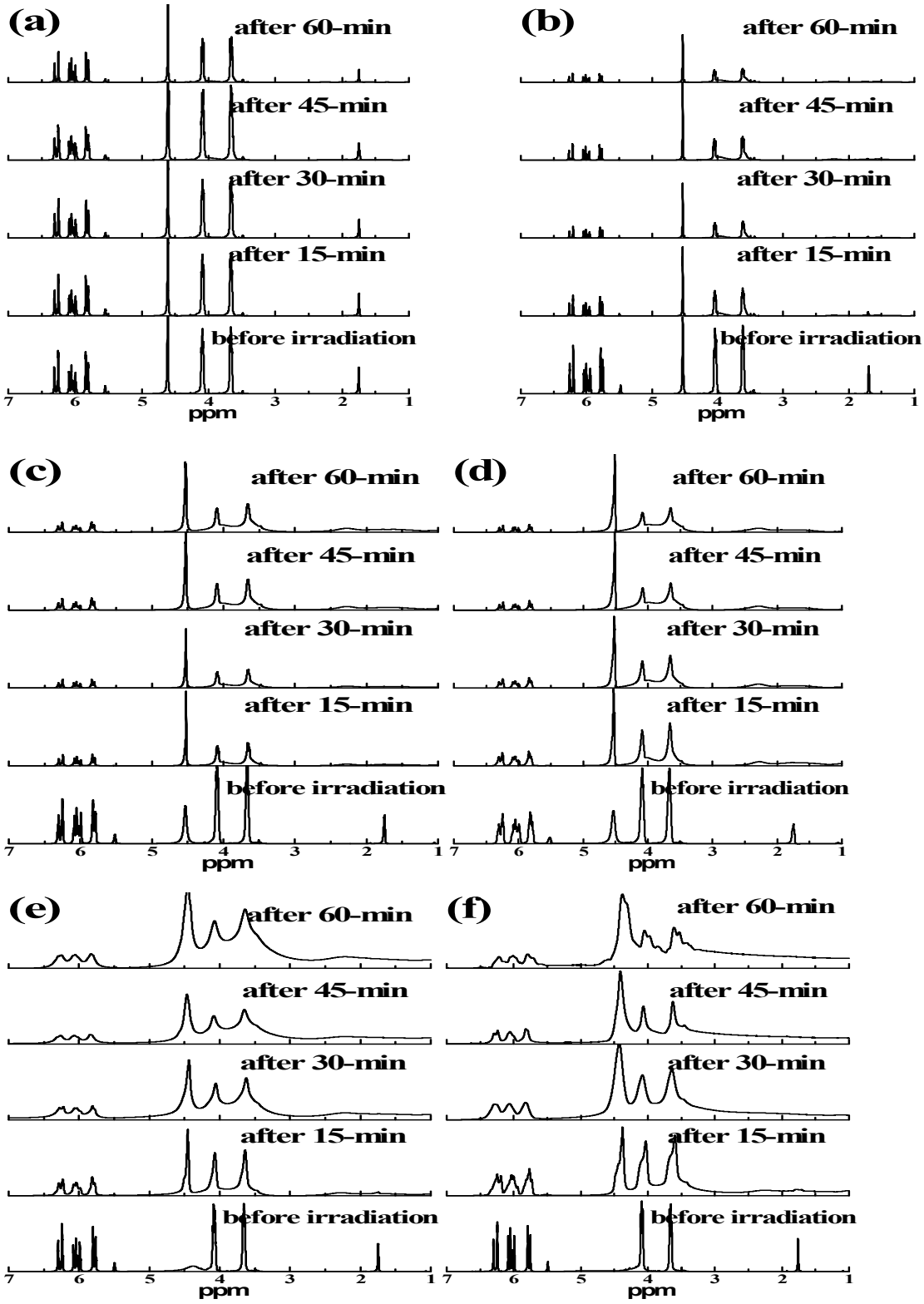


Figure S7 ^{1}H NMR spectra of HEA as a function of different ratios of HEA/D_2O mixtures without *d*-DMSO after N_2-bubbling and in the presence of CBS X/IOD PIS before and after LED exposure. The volume ratios of HEA/D_2O range from (a)1/5, (b) 1/2, (c) 1/1, (d) 2/1, (e) 5/1 to (f) 11/1. [CBS X] = 3.6 mM; [IOD] = 4.8 mM.