Supporting Information

Addressing the role of triphenylphosphine in copper catalyzed ATRP

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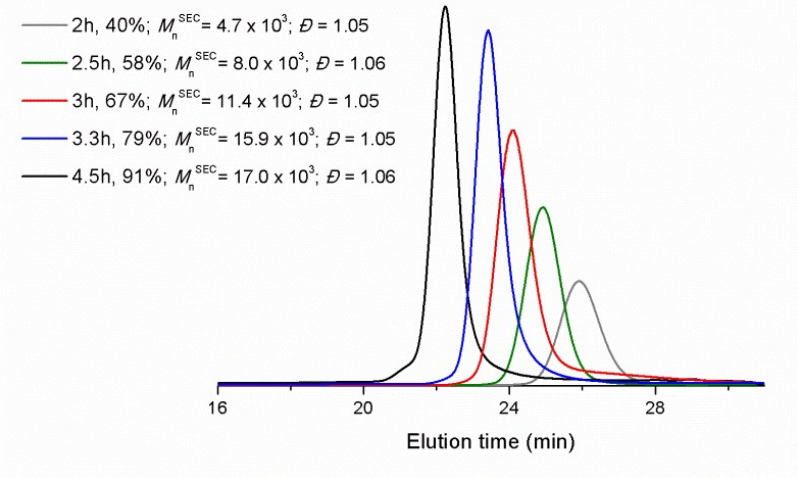

Figure S1: SEC traces with conversion for the SARA ATRP of MA mediated by PPh_3 in DMSO/H_2O = 90/10 (v/v) at 50 °C. Reaction conditions: $[MA]_0/[solvent]$ = 2/1 (v/v); $[MA]_0/[EBiB]_0/[PPh_3]_0/ [Cu^{II}Br_2]_0/ [Me_6TREN]_0$= 222/1/1/0.1/1.1.

Table S1: SARA ATRP of MA mediated by PPh_3 in DMSO (or DMSO/H_2O = 90/10 (v/v)), using different $[PPh_3]_0/[CuBr_2]_0/[Me_6TREN]_0$ ratios [a].

entry	solvent	initiator	T (°C)	$[PPh_3]_0/[Cu^{II}Br_2]_0$ /$[Me_6TREN]_0$	time (h)	conv (%)	k_p^{app} (h^{-1})	$M_n^{th} \times 10^{-3}$	$M_n^{SEC} \times 10^{-3}$	$Đ$
1	Acetonitrile	EBiB	30	1/0.1/1.1	24	10	---	1.90	2.10	1.16
2	DMF	EBiB	50	1/0.1/1.1	24	30	---	5.7	6.9	1.05
3	Ethanol	EBiB	50	1/0.1/1.1	9	96	---	18.6	23.4	1.28
4	DMSO/H_2O	EBiB	50	1/0.1/1.1	4.5	91	0.761	16.4	16.96	1.06
5	DMSO/H_2O	EBPA	50	1/0.1/1.1	15	82	---	14.8	38.8	1.08
6	DMSO/H_2O	EBiB	50	1/0.1/0.2	24	90	---	15.78	16.75	1.07
7	DMSO/H_2O	EBPA	50	1/0.1/0.2	24	76	---	14.5	21.62	1.02

[a] Conditions: $[MA]_0/[solvent]$ = 2/1 (v/v); $[initiator]_0/[MA]_0$ = 1/210.

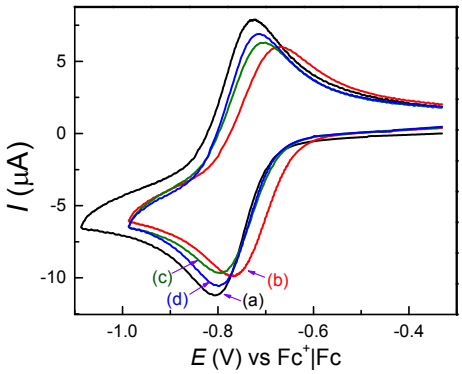

Figure S2: Cyclic voltammetry of $[BrCu^{II}Me_6TREN]^+$ in DMSO + 0.1 M Et_4NBF_4 at 50 °C, recorded on GC electrode at 0.2 V/s: (a) 1.0 mM $[BrCu^{II}Me_6TREN]^+$; (b) as (a) + 1 mM PPh_3; (c) as (b) + 10 mM Et_4NBr; (d) as (b) + 100 mM Et_4NBr.

Table S2: SEC parameters over time, determined by multidetector calibration, for the SARA ATRP of MA mediated by PPh_3 in DMSO/H_2O = 90/10 (v/v) at 50 °C. Reaction conditions: $[MA]_0/[solvent]$ = 2/1 (v/v); $[MA]_0/[EBiB]_0/[PPh_3]_0/ [Cu^{II}Br_2]_0/ [Me_6TREN]_0$= 210/1/1/0.1/1.1.

	Reaction in the presence of light		**Reaction in the dark**	
Time (h)	M_n^{SEC} **x 10^{-3}**	**Đ**	M_n^{SEC} **x 10^{-3}**	**Đ**
1.50	2.66 [a]	1.03 [a]	2.50 [a]	1.11 [a]
2.00	6.01	1.08	5.28	1.11
2.50	10.03	1.05	9.04	1.06
3.00	13.64	1.05	12.47	1.04
3.50	17.07	1.09	15.43	1.10
4.00	19.78	1.08	19.27	1.10

[a] determined by universal calibration.

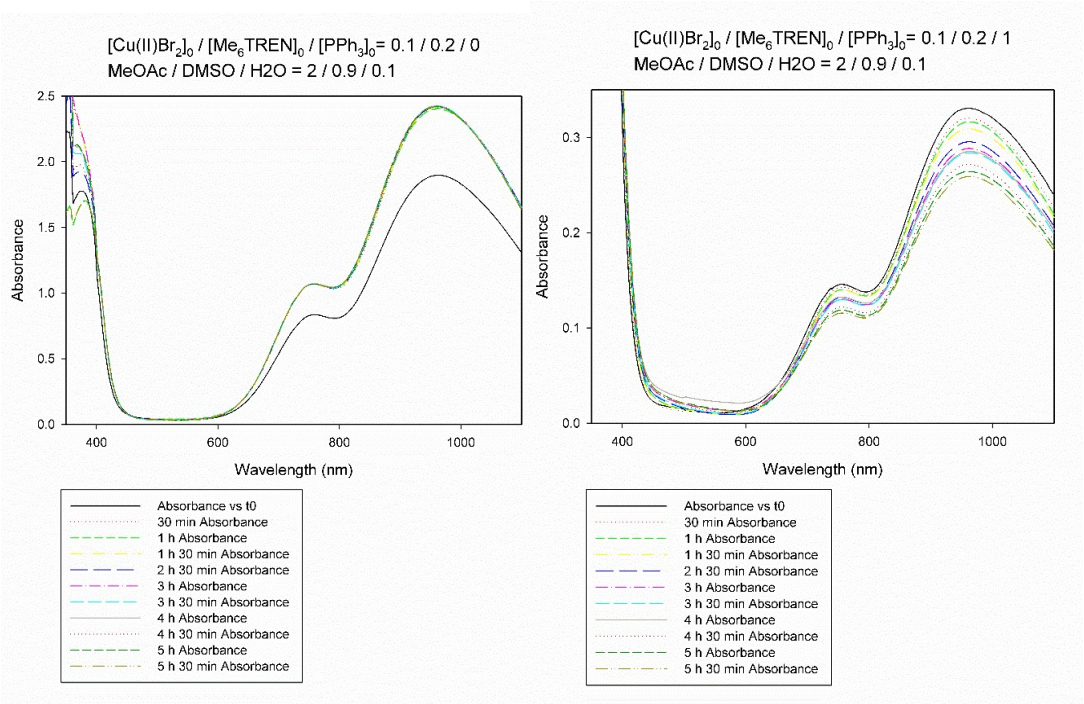

Figure S3: UV-Vis spectra of $Cu^{II}Br_2/Me_6TREN$ in a MeOAc/DMSO/H_2O = 2/0.9/0.1 (v/v/v) mixture at 50 ºC in the absence and in the presence of PPh_3. Conditions: $[CuBr_2]_0/[Me_6TREN]_0/[PPh_3]_0$ = 0.1/0.2/0 (molar ratio), $[Cu^{II}Br_2]_0$ = 3.35 m (left); and $[CuBr_2]_0/[Me_6TREN]_0/[PPh_3]_0$ = 0.1/0.2/1 (molar ratio), $[Cu^{II}Br_2]_0$ = 3.35 m (right).

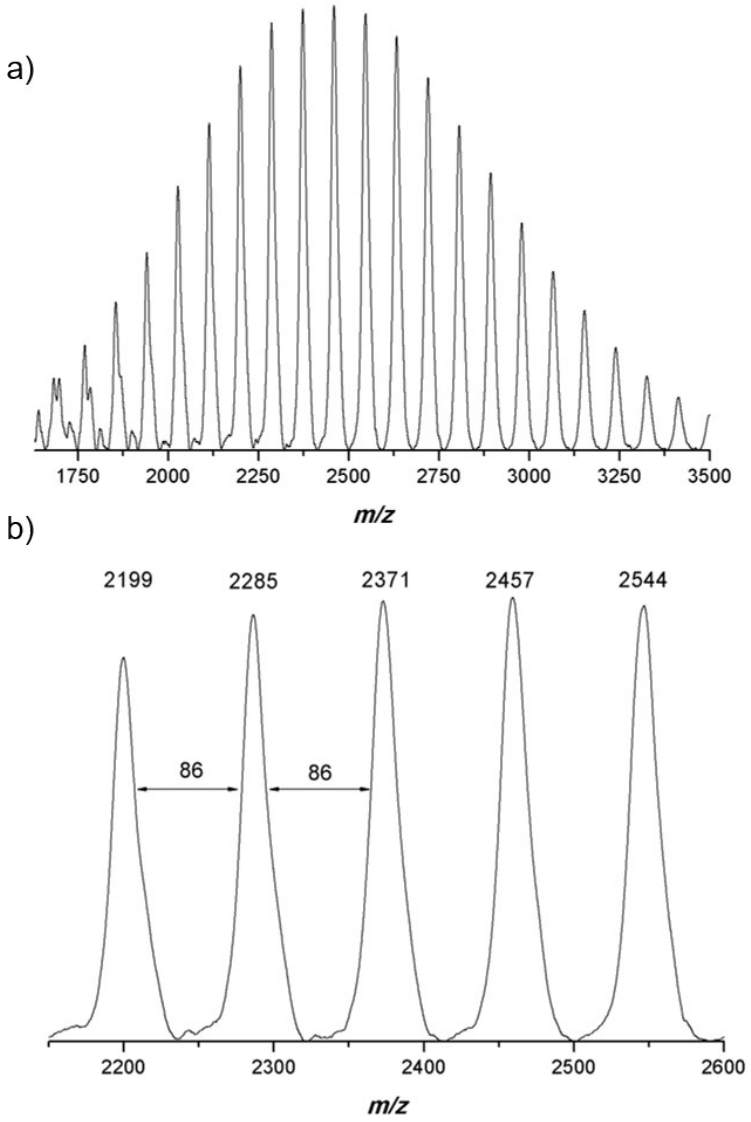

Figure S4: MALDI-TOF-MS in the linear mode (using HABA as matrix) a) from m/z 1600 to 3500 and b) enlargement of the spectrum from m/z 2150 to 3600 of PMA-Br ($M_n^{SEC} = 2.5\times10^3$; $Đ = 1.02$).

Table S3: MALDI-TOF MS peaks assignment.

n	MW_{th}[a]	MW_{exp} (Figure S3)
23	2198	2199
24	2284	2285
25	2371	2371
26	2457	2457
27	2543	2544

[a] $MW_{th} = M(EBiB) + n\times M(MA) + M(Na^+)$