Supporting Information for

Deep eutectic solvents for green and efficient iron-mediated ligand-free atom transfer radical polymerization

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Polymerization Data:

Table. S1 The chemical shifts with different ratios of DESs.

DESs	Chemical shift (ppm)						
	0:3	1:3	2:3	3:4	3:2	3:1	3:0
[a]TBABr:Gly	4.498	4.489	4.483	4.478	4.476	4.474	NA
[b]Ac:KSCN	7.354	7.335	7.306	7.305	7.298	7.294	NA
[c]CPL:Ac	6.731	6.720	6.706	6.704	6.698	6.694	NA

[a]The chemical shifts of OH in Glycerol; [b]The chemical shifts of NH_2 in Acetamide; [c]The chemical shifts of NH_2 in Acetamide.

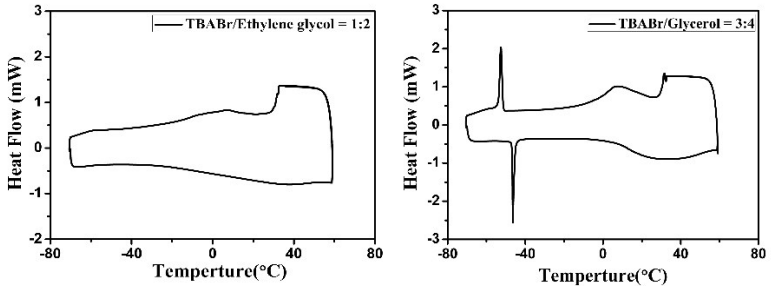

Figure S1. Melting point of TBABr:EG 1:2 and TBABr:Gly 3:4 detected by differential scanning calorimetry (DSC).

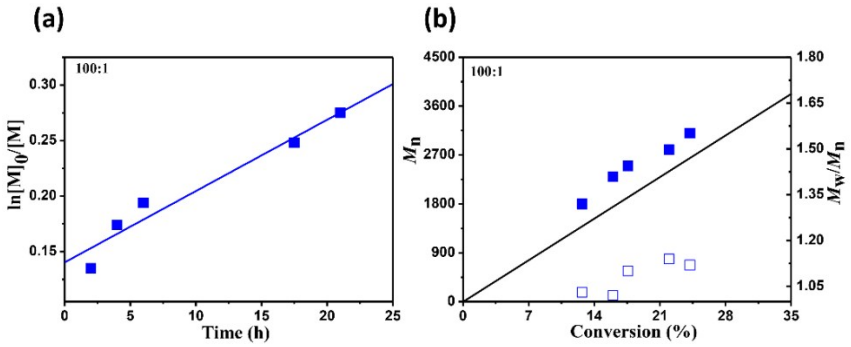

Figure S2. ln([M]$_0$/[M]) as a function of time (a) and evolution of number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for ATRP of MMA with trace amount of DES. Polymerization conditions (a) [MMA]$_0$:[FeBr$_2$]$_0$:[EBPA]$_0$ = 100:1:1, MMA/DES(v/v) =100:1 without any additional ligand, 60 °C.

Table. S2 Redox potentials of $FeBr_2$ with different types of additives measured in methanol.

entry	Additives	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)	$E_{1/2}$ (V)
1	EG	0.752	0.999	0.247	o.876
2	Urea	0.754	0.997	0.243	0.875
3	TBABr/EG	0.756	0.994	0.238	0.873
4	ChCl/EG	0.798	0.940	0.142	0.869
5	Urea/CPL	0.751	1.005	0.254	0.878
6	Urea/Acetamid e	0.765	0.991	0.226	0.878

[FeBr$_2$]$_0$/[Additives]$_0$ = 1:2, DES =64 μL. E_{pa} and E_{pc} are the peak potentials of the oxidation and reduction waves, respectively. $\Delta E_p = E_{pa} - E_{pc}$, $E_{1/2} = (E_{pa} + E_{pc})/2$.

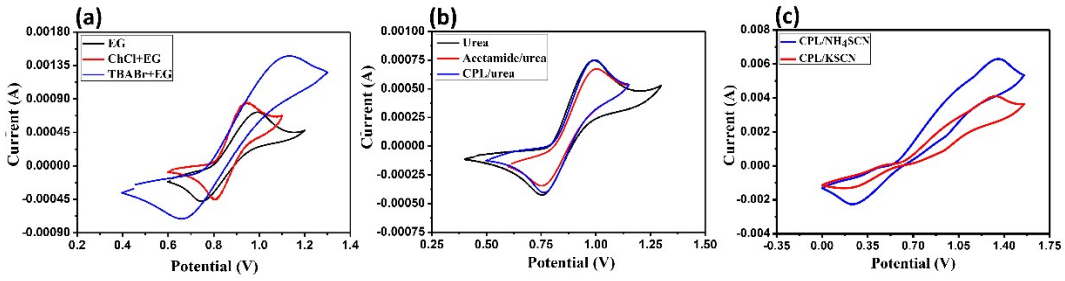

Figure S3. Cyclic voltammograms (50mV/s) of $FeBr_2$ (1.2mM) with different types of additives as the ligands in methanol at room temperature. $[Et_4NBF_4]$ = 0.1M (supporting electrolyte). $[DES]_0$ = 64 uL, $[FeBr_2]_0$/[additives] = 1:2.