Supporting Information

Investigating Anisole/Cu(II)-Macroligand-complex Pair to Broaden Solubility Scope and Catalyst Recycling for Atom Transfer Radical Polymerization

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Materials

Methyl methacrylate (MMA, ≥ 99%, Shanghai Macklin Biochemical Co. Ltd), was purified by passing through a column packed with activated neutral alumina. 2,2- azobisisobutyronitrile (AIBN, ≥ 97%, Tianjin Guanfu Fine Chemical Research Institute) was purified from ethanol, dried and then stored in a refrigerator at about -2 ℃. Other chemical reagents such as poly(ethylene glycol)-300-methyl ether methacrylate ($PEG_{300}MMA$) (Macklin, China), ethyl bromide (99%, Yonghua Chemical Co. Ltd), ethyl 2-bromoisobutyrate (EBiB, 98%, Energy Chemical, China), acrylolyl chloride (96%), 2-[(dimethylamino)ethyl] methacrylate (99%), ethanolamine (97%), acetonitrile (+99.9 analytical grade), benzene (+99%), 1,3,5-trimethylbenzene (97%), dimethyl sulfoxide (DMSO, analytical grade), triethylamine (99%), anisole (99%), acetonitrile (99%) were all acquired from Shanghai Macklin Biochemical Co. Ltd, while 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine·HCl (98%, Shanghai Yuanye Bio-Technology Co. Ltd), copper(II)bromide ($CuBr_2$, 99.95%, Aladdin Chemistry Co. Ltd), anhydrous methanol (+99.5%), toluene (≥ 99.5%), tetrahydrofuran (THF, +99.5%), dichloromethane (+97.5%) from Sinopharm Chemical Reagent Co. Ltd,, anhydrous sodium carbonate (+99.8%), anhydrous potassium carbonate (+99%), anhydrous magnesium sulphate (+99%), xylene (≥ 99.0%) from Shanghai Lingfeng Chemical reagent Co. Ltd., were all used as received.

Characterization

The dispersity (M_w/M_n) and number-average molecular weight ($M_{n,GPC}$) of the polymers were analyzed using an Agilent Technologies PL-220 gel permeation chromatography (GPC) system equipped with a refractive index detector. Separation was performed on a PLgel 5 µm MIXED-C column (300×7.5 mm) with a molecular weight detection ranging from 6×10^2 to 5×10^5 g/mol. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min and a temperature of 40 ℃. The sample injection was carried out automatically using an Agilent Technologies autosampler, and the system was calibrated with polystyrene standards. The obtained polymers were further characterized by ^1H NMR spectroscopy on an INOVA 600 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvents with tetramethylsilane (TMS) as the internal reference. The residual copper content in the polymer solutions was determined by inductively coupled plasma mass spectrometry (ICP-MS). The polymerization mechanism was investigated using a Shimadzu UV-2600 UV–Vis spectrometer over a wavenumber range of 200–900 cm^{-1}.

Equation S1: Calculating the percentage conversion of monomer

% conv = (1 - ratio volume of $M_{[rxn]}$ × peak area of V_H × ratio volume of $A_{[rxn]}$) × 100%

where;

$M_{[rxn]}$ = Mononer reaction mixture

V_H = Vinyl Hydrogen of Monomer after polymerization

$A_{[rxn]}$ = Anisole before/after reaction

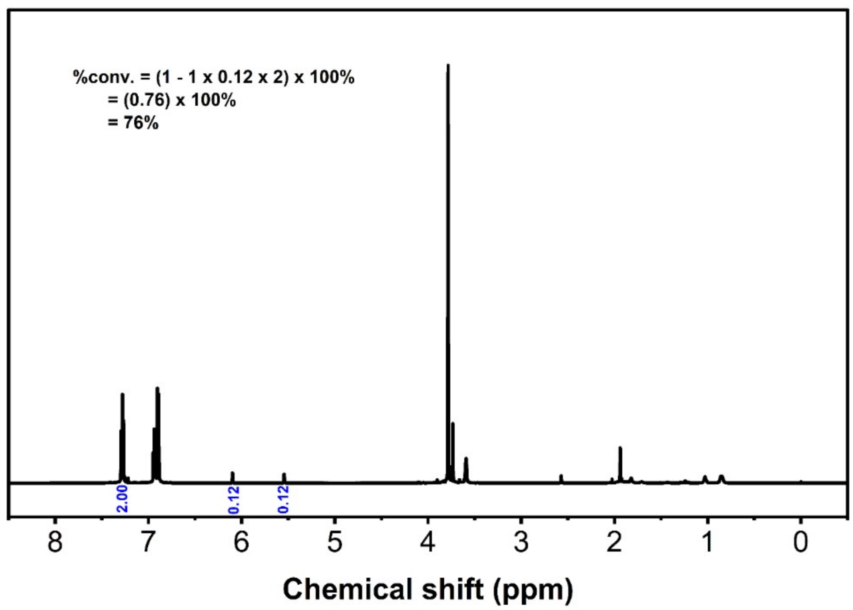

Fig. S1 [1]H NMR spectrum of the representative polymerization reaction mixture used in all the calculations for the percentage conversion

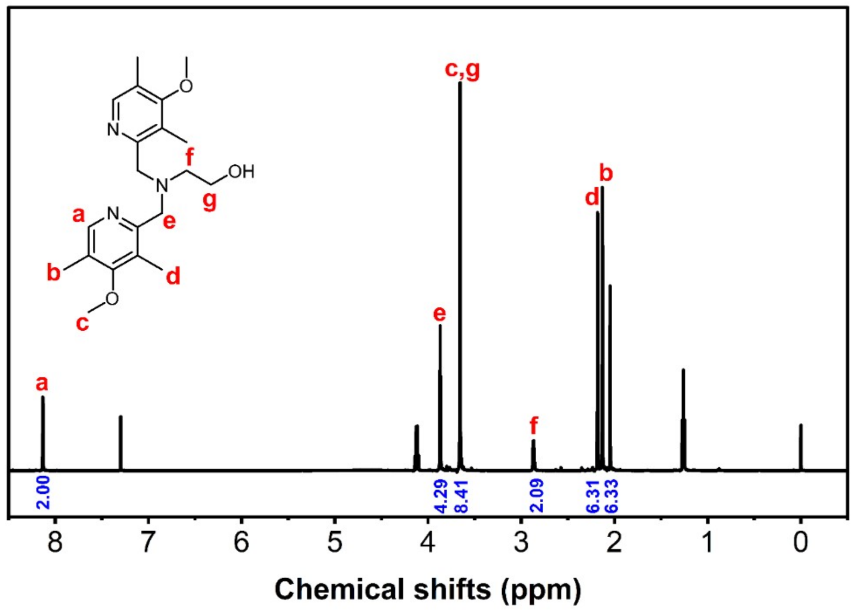

Fig. S2 [1]H NMR analysis of intermediate product **1** performed in $CDCl_3$ employing TMS as an internal reference

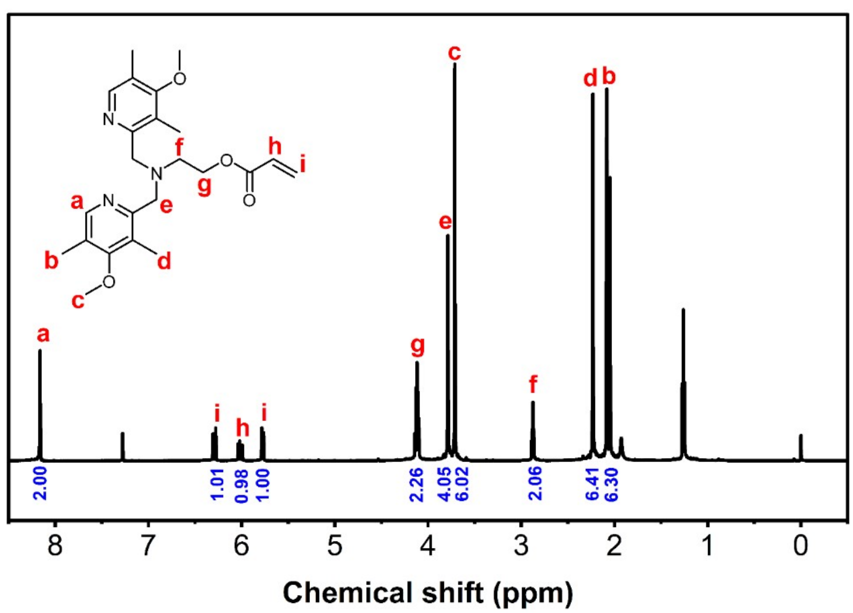

Fig. S3 [1]H NMR analysis of intermediate product **2** performed in $CDCl_3$ employing TMS as an internal reference

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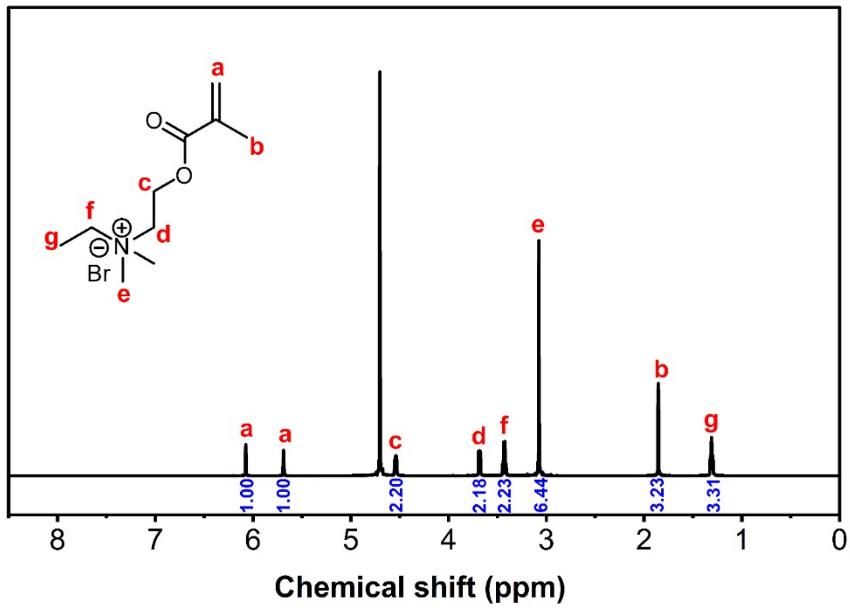

Fig. S4 ^{1}H NMR analysis of intermediate product **3** performed in D_2O employing TMS as an internal reference

Table S1 Different batches of $PEG_{300}MMA$ obtained from the same company and their ratios to attain the TPSC-based ICAR ATRP system

Entry	Company	Anisole (mL)	MMA (mL)	$CuBr_2$ (mg)	AIBN (mg)	MA-sLN	ILM	PEG300 MMA	rt[a]	80 °C	rt[b]	No. of Batches
1	Macklin[a]	2.0	1.0	1.0	7.8	1	4.2	5.0	M	M	I	18
2	Macklin[b]	2.0	1.0	1.0	7.8	1	3.2	5.0	M	M	I	4
3	Macklin[c]	2.0	1.0	1.0	0.0	1	2.9	5.0	M	M	I	3

I = Immiscibility and M = Miscibility; rt[a] = At room temperature and rt[b] = After Cooling cycle to room temperature; [a,b,c] $PEG_{300}MMA$ batches

Table S2 Sustainability assessment guide of 4 selected organic solvents based on safety, health, and environmental scores[1-3]

Entry	Solvent	Boiling point (°C)	Safety score	Healthy score	Environmental score	Solvent sustainability ranking	Overall score
1	Anisole	154	4	1	5	Recommended	1
2	Benzene	80	6	10	3	Hazardous	4
3	Xylene	140	4	2	5	Problematic	2
4	Toluene	111	5	6	3	Problematic	3

The color code represents the scoring index: green for 1–3, yellow for 4–6, and red for 7–10

Table S3 Effects of varying Macroligand (PILLL1) for TPSC-based ICAR ATRP system

Entry	x	x (mg)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	5	279	4	80	16200	13700	1.36
2	4	223	4	88	17800	13400	1.09
3	3	167	4	74	15000	13000	1.20
4	2	112	4	72	14600	14100	1.13
5	1	56	4	68	13800	11600	1.27

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/1/x/1, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$

Table S4 Effects of varying AIBN for TPSC-based ICAR ATRP system

Entry	x	x (mg)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	1.25	0.980	4	92	18600	15300	1.11
2	1.00	0.780	4	88	17800	13400	1.09
3	0.50	0.390	4	68	13800	12600	1.14
4	0.25	0.195	4	40	8200	7400	1.16
5	0.10	0.078	4	*	*	*	*

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/1/4/x, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$.
*No polymer formed

Table S5 Effects of varying $CuBr_2$ for TPSC-based ICAR ATRP system

Entry	x	x (mg)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	1.00	10.4	4	88	17800	13400	1.09
2	0.50	5.2	4	80	16200	10500	1.21
3	0.25	2.6	4	92	18600	16900	1.25
4	0.13	1.3	4	90	18200	15500	1.13

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/1/4/1, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$

Table S6 Effects of varying volume of solvent for TPSC-based ICAR ATRP system

Entry	Anisole (x) (mL)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	3.0	4	82	16600	13700	1.30
2	2.5	4	75	15200	13500	1.35
3	2.0	4	88	17800	13400	1.09

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/1/4/1, V_{MMA} = 1 mL, $V_{anisole}$ = x mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$

Table S7 Effects of varying Temperature for TPSC via ICAR ATRP system

Entry	Temperature (x) (℃)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	70	4	65	13200	10700	1.28
2	80	4	88	17800	13400	1.09
3	90	4	87	17600	15900	1.16

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/1/4/1, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = x ℃. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$

Table S8 Effects of varying alkyl halide initiator (EBiB) for TPSC-based ICAR ATRP system

Entry	x	x (μL)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	1.5	10.2	4	82	11100	13100	1.18
2	1.0	6.8	4	88	17800	13400	1.09
3	0.5	3.4	4	76	30400	21700	1.43

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/x/1/4/1, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 ℃. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$

Table S9 Recycling performance of the PILLL1/$CuBr_2$ catalyst in TPSC-based ICAR ATRP system

Entry	Recycling times	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	CR[a] (ppm)
1	1	7	64	13000	18000	1.40	187
2	2	7	52	10600	17400	1.38	114
3	3	7	16	3400	*	*	*

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/0.1/1.2/0.2, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times$ Conv.% + $M_{w,EBiB}$. CR[a] refers to the residual catalyst present in the organic polymer solution phase, measured by ICP-MS. *No monomer formed, and the reaction mixture became homogeneous

Table S10 Recycling performance of the PILLL1/$CuBr_2$ catalyst in TPSC-based ICAR ATRP system under varied time and AIBN concentration

Entry	Recycling times	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	CR[a] (ppm)
1	1	7	64	13000	41300	1.37	34.5
2	2	6	84	17000	84100	1.31	32.9
3	3	5	85	17200	68300	1.20	28.9
4	1*	7	65	13200	45600	1.55	17.5
5	2*	6	83	16800	83500	1.27	16.7
6	3*	5	84	17000	94100	1.24	14.2

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/0.1/4/x = 0.2,0.3, 0.4, and *$[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/0.05/4/x = 0.2, 0.3, 0.4, V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times$ Conv.% + $M_{w,EBiB}$. CR[a] refers to the residual catalyst present in the organic polymer solution phase, measured by ICP-MS

Table S11 Recycling performance of the PILLL1/$CuBr_2$ catalyst in TPSC-based ICAR ATRP system under varied time and AIBN concentration

Entry	Recycling times	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	CR[a] (ppm)
1	1[a]	7	68	13800	45300	1.58	10.3
2	2[b]	6	80	16200	41000	1.48	9.0
3	3[c]	5	88	17800	35500	1.48	5.8
4	4[c]	5	88	17800	30500	1.44	4.4
5	5[c]	5	84	17000	33000	1.25	3.4

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/0.025/4/x = 0.2[a], 0.3[b], 0.4[c], V_{MMA} = 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C. $M_{n,th} = ([M]_0/[M]) \times [MMA] \times Conv.\% + M_{w,EBiB}$. CR[a] refers to the residual catalyst present in the organic polymer solution phase, measured by ICP-MS

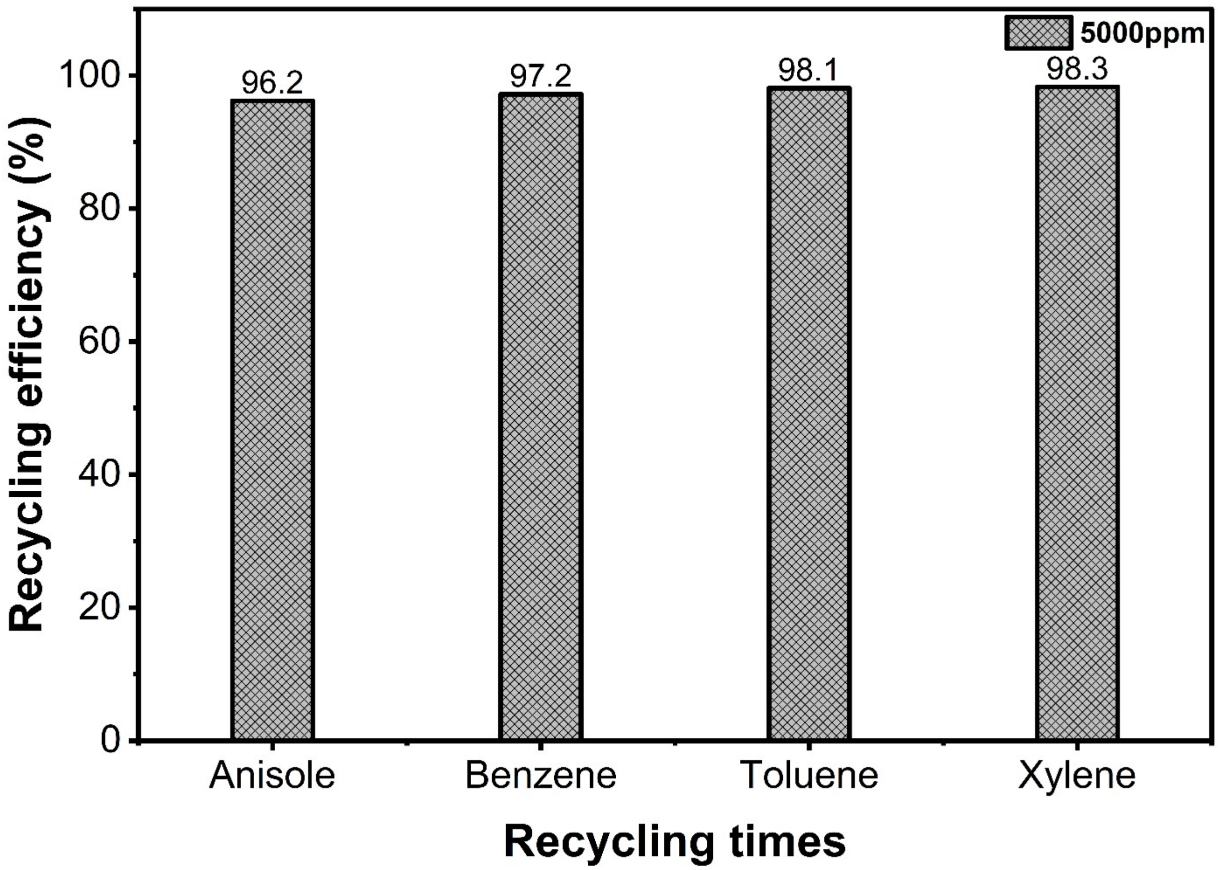

Fig. S5 Recycling efficiency represented as a percentage of residual copper catalyst retained in the PILLL1 phase relative to initial copper catalyst content, determined by ICP–MS, in four different solvents. Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PILLL1]_0/[AIBN]_0$ = 200/1/1/4/1, V_{MMA}= 1 mL, $V_{anisole}$ = 2 mL, temperature = 80 °C

References

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3. C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chemistry*, 2016, **18**, 3879-3890.