Electronic Supplementary Information

Poly-quasi-eutectic solvents (PQESs): versatile solvent for dissolving metal oxides

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Fig. S8 The dissoving of CoO in the synthesized PQESs: (a) Photographs of PQESs after dissolving CoO; (b) solubility of CoO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

Fig. S9 The dissoving of NiO in the synthesized PQESs: (a) Photographs of PQESs after dissolving NiO; (b) solubility of NiO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

Fig. S10 The dissoving of CuO in the synthesized PQESs: (a) Photographs of PQESs after dissolving CuO; (b) solubility of CuO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

Fig. S11 The dissoving of ZnO in the synthesized PQESs: (a) Photographs of PQESs after dissolving ZnO; (b) solubility of ZnO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

Fig. S12 The dissoving of Al_2O_3 in the synthesized PQESs: (a) Photographs of PQESs after dissolving Al_2O_3; (b) solubility of Al_2O_3 in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

Fig. S13 The dissoving of CaO in the synthesized PQESs: (a) Photographs of PQESs after dissolving CaO; (b) solubility of CaO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

Fig. S14 Relationship of metal oxides (Fe_2O_3, CoO, NiO, CuO, ZnO, Al_2O_3, and CaO) solubility vs α value for PEG-based PQESs. The lines are the linear fitting results of the solubility vs α value.

Fig. S15 Relationship of metal oxides (Fe_2O_3, CoO, NiO, CuO, ZnO, Al_2O_3, and CaO) solubility vs T_m (a), viscosity (b), and conductivity (c) values for PEG-based PQESs. The lines are the linear fitting results of the solubility vs T_m (a), viscosity (b), and conductivity (c) values.

Fig. 16 TEM images of ZnO dissolved in 2-furonic acid-PEG at low (a) and high (b) magnification.

Fig. S17 ^{1}H NMR spectra of before (black) and after (red) metal oxides dissolved in the synthesized PQESs: (a) CaO in 2-furoic acid-PEG and (b) CuO in thiourea-PEG.

Reference

Table S1 The onset melting temperature (T_m) of PQESs. [a] means no data. [b] means the data was derived from reference 1.

PQESs HBDs	T_m (°C)				
	PEG 200	PEG 1000	P123 5800	PPG-NH_2 250	DMPEG D-230
2-furoic acid	-71.8	29.8	27.2	-93.0	-70.2
oxalic acid	-66.9	30.4	26.8	-85.8	-67.2
malonic acid	-69.2	29.2	28.6	-89.9	-[a]
succinic acid	-73.2	29	27.5	-90.1	-[a]
glutaric acid	-76.7	27.8	26.9	-90.4	-[a]
acetamide	-78.6	31.2	26.9	-95.2	-73.3
urea	-64.2	32.4	29.6	-94.3	-57.8
N-methylurea	-70.8	31.2	27.6	-96.2	-73.4
thiourea	-65.1[b]	29.6	27.6	-89.7	-64.0
N-methylthiourea	-67.6	29.4	26.5	-91.2	-62.5
N,N-dimethylthiourea	-75.6	29.3	25.7	-93.2	-59.8

Table S2 Temperature dependent viscosity of PQESs. [a] means no data.

PQESs / HBDs	η (mPa·s)							
	Temperature (K)							
	298.15	**308.15**	**318.15**	**328.15**	**338.15**	**348.15**	**358.15**	**368.15**
2-furoic acid	87.3	48.8	30.0	19.8	13.8	10.3	7.74	5.99
oxalic acid	123	86.2	50.7	32.9	22.3	15.9	11.8	-[a]
malonic acid	118	65.1	39.1	25.3	17.4	12.7	9.69	7.87
succinic acid	95.2	54.5	33.9	22.5	15.8	11.6	8.88	7.01
glutaric acid	92.7	56.5	34.8	24.8	16.7	12.0	8.96	6.30
acetamide	46.1	27.8	18.6	12.9	9.41	7.11	5.46	3.95
urea	114	60.2	35.4	22.8	15.6	11.3	8.57	6.77
N-methylurea	74.5	42.4	26.2	17.6	12.5	9.21	7.19	5.67
thiourea	170	72.6	41.5	25.9	17.5	12.8	9.41	7.21
N-methylthiourea	118	66.5	37.6	26.3	16.6	11.6	8.51	5.60
N,N-dimethylthiourea	59.6	34.1	21.8	14.8	10.5	7.85	6.01	4.18

Table S3 Temperature dependent conductivity of PQESs. [a] means no data.

PQESs / HBDs	σ (μS·cm^{-1})							
	Temperature (K)							
	298.15	**308.15**	**318.15**	**328.15**	**338.15**	**348.15**	**358.15**	**368.15**
2-furoic acid	4.21	5.59	7.70	10.1	13.0	15.7	18.1	21.1
oxalic acid	5.44	7.95	10.4	13.4	16.6	20.0	-[a]	-[a]
malonic acid	1.21	1.57	2.01	2.66	3.40	4.36	5.16	5.97
succinic acid	1.11	1.36	1.90	2.50	3.16	3.99	4.69	5.58
glutaric acid	4.24	6.39	9.14	11.4	14.4	18.1	20.9	24.5
acetamide	5.16	6.87	9.28	11.3	14.1	17.1	19.5	22.8
urea	2.78	4.08	5.91	7.99	10.2	13.8	18.0	25.1
N-methylurea	10.1	13.1	20.2	26.6	34.2	41.6	48.9	62.6
thiourea	2.72	3.40	4.73	6.91	9.28	12.2	14.7	18.3
N-methylthiourea	4.20	7.21	10.0	13.7	18.8	25.4	35.0	43.8
N,N-dimethylthiourea	4.33	6.41	10.0	13.8	18.1	24.8	32.7	44

Table S4 Energy for activation of viscous flow E_η and conductivity E_Λ obtained by fitting the data in Figure S3 to equation 1 and those in Figure S4 to equation 2.

PQESs **HBDs**	**ln η_0**	**E_η** **kJ·mol^{-1}**	**ln σ_0**	**E_σ** **kJ·mol^{-1}**
2-furoic acid	-9.57±0.4	34.5±1.1	10.1±0.1	-21.6±0.5
oxalic acid	-9.21±0.2	34.8±0.7	10.7±0.2	-22.1±0.6
malonic acid	-9.32±0.3	34.5±2.0	10.3±0.3	-25.8±0.9
succinic acid	-9.20±0.4	33.8±1.1	9.00±0.1	-22.1±0.4
glutaric acid	-9.42±0.3	34.4±0.9	10.5±0.2	-22.2±0.6
acetamide	-8.85±0.3	31.2±0.8	9.40±0.1	-19.0±0.3
urea	-10.1±0.5	36.5±1.5	12.2±0.2	-27.8±0.3
methylurea	-9.24±0.4	33.3±1.2	11.8±0.2	-23.6±0.6
thiourea	-12.9±0.4	40.3±1.1	11.3±0.1	-25.8±0.4
N-methylthiourea	-10.9±0.3	38.9±1.0	13.5±0.1	-29.8±0.4
N,N-dimethylthiourea	-9.57±0.4	33.6±1.1	13.6±0.2	-30.1±0.4

Table S5 Comparison of solubility of 7 metal oxides in our PEG-based PQESs and other reported ionic liquids. [a][P_{66614}][Cl]: trihexyl(tetradecyl)phosphonium chloride; [b][C_2mim][Cl]: 1-ethyl-3-methylimidazolium chloride; [c][C_2mim][OAc]: 1-ethyl-3-methylimidazolium acetate; -[d] means no data.

PQESs	**Solubility (ppm unless stated otherwise)**							
HBDs	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**Al_2O_3**	**CaO**	**Reference**
2-furoic acid	123	1995	143	818	**18139**	218	**3170**	our work
oxalic acid-PEG	**1763**	-[d]	-[d]	1.8	-[d]	**324**	155	our work
thiourea-PEG	-[d]	370	45.8	**1303**	181	261	1024	our work
ChCl-malonic acid	376	3626	151	14008	16217	-[d]	-[d]	[2]
ChCl-urea	49	-	325	470	8466	<1	6	[3]
[a][P_{66614}][Cl]–HCl	647	993	996	1035	1041	-[d]	698	[4]
[b][C_2mim][Cl]	-[d]	-[d]	5 mg/g	64 mg/g	36 mg/g	-[d]	-[d]	[5]
[c][C_2mim][OAc]	-[d]	-[d]	0.9 mg/g	2.3 mg/g	83 mg/g	-[d]	-[d]	[5]

Table S6 The solvatochromic parameters of PEG-based PQESs.

PQESs	α	β	π^*
2-furoic acid-PEG	2.9694	0.7584	0.9433
oxalic acid-PEG	3.4820	1.4406	0.8497
malonic acid-PEG	3.0940	1.1118	0.9053
succinic acid-PEG	2.7790	1.4080	0.9053
glutaric acid-PEG	2.8421	1.1685	0.8881
acetamide-PEG	2.5653	1.8427	0.9640
urea-PEG	2.6539	1.8552	1.0013
N-methylurea-PEG	2.5566	1.9783	0.9640
thiourea-PEG	2.6828	1.5976	1.0383
N-methylthiourea-PEG	2.7722	1.5757	1.0013
N,N-dimethylthiourea-PEG	2.7134	1.6989	0.9640

Table S7 The adjusted R^2 of solubility of Fe_2O_3, CoO, NiO, CuO, ZnO, Al_2O_3, and ZnO vs α, T_m, viscosity, and conductivity values of different PEG-based PQESs.

Metal oxides in PEG-based PQESs	Adjusted R^2			
	α	*Tm*	Viscosity	Conductivity
Fe_2O_3	0.6268	0.3591	0.2789	0.0016
CoO	0.4032	0.0013	0.1396	0.0219
NiO	0.4379	0.1091	0.0001	0.0053
CuO	0.6215	0.0062	0.0001	0.0024
ZnO	0.0870	0.0303	0.0002	0.1678
Al_2O_3	0.1768	0.6837	0.4194	0.0022
CaO	0.0193	0.0073	0.0194	0.0477

Table S8 Symmetric vibrations($\nu_s(COO^-)$), antisymmetric stretching vibrations, ($\nu_{as}(COO^-)$), and ditance between them of carboxylic acid-based PQESs after dissolving metal oxides.

Metal oxides dissolving in PQESs	$\nu_{as}(COO^-)$ cm^{-1}	$\nu_s(COO^-)$ cm^{-1}	$\nu_{as}(COO^-)$-$\nu_{as}(COO^-)$ cm^{-1}
Fe_2O_3 in oxalic acid-PEG	1743	1456	287
CoO in 2-furoic acid-PEG PQES	1713	1474	239
NiO in malonic acid-PEG PQES	1737	1459	278
ZnO in 2-furoic acid-PEG	1734	1477	257
Al_2O_3 in oxalic acid-PEG PQES	1740	1456	284
CaO in 2-furoic acid-PEG	1722	1477	245

Table S9 pK_a values of the selected carboxyl acid-based HBDs.

Carboxyl acid-based HBDs	pK_{a1}	pK_{a2}
2-furoic acid	3.16	-[a]
oxalic acid	1.27	4.27
malonic acid	2.85	5.66
succinic acid	4.21	5.64
glutaric acid	3.77	6.08

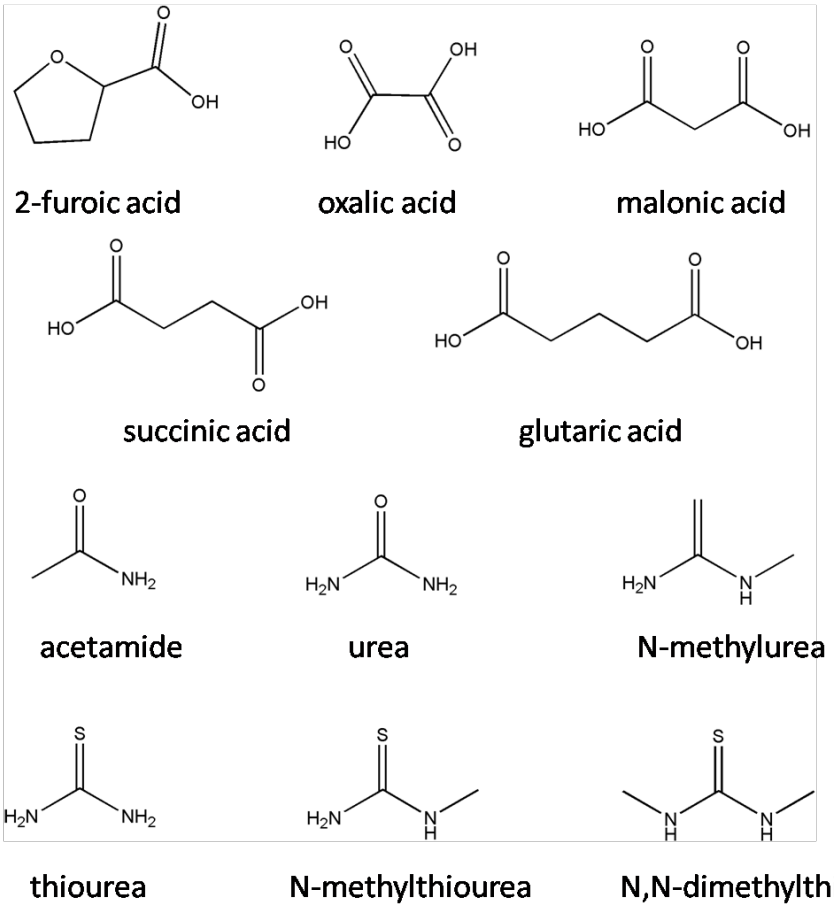

Fig. S1 Structures of the selected 11 hydrogen bonding donors (HBDs): 2-furoic acid, oxalic acid, malonic acid, succinic acid, and glutaric acid, acetamide, urea, N-methylurea, thiourea, N-methylthiourea, and N,N-dimethylthiourea.

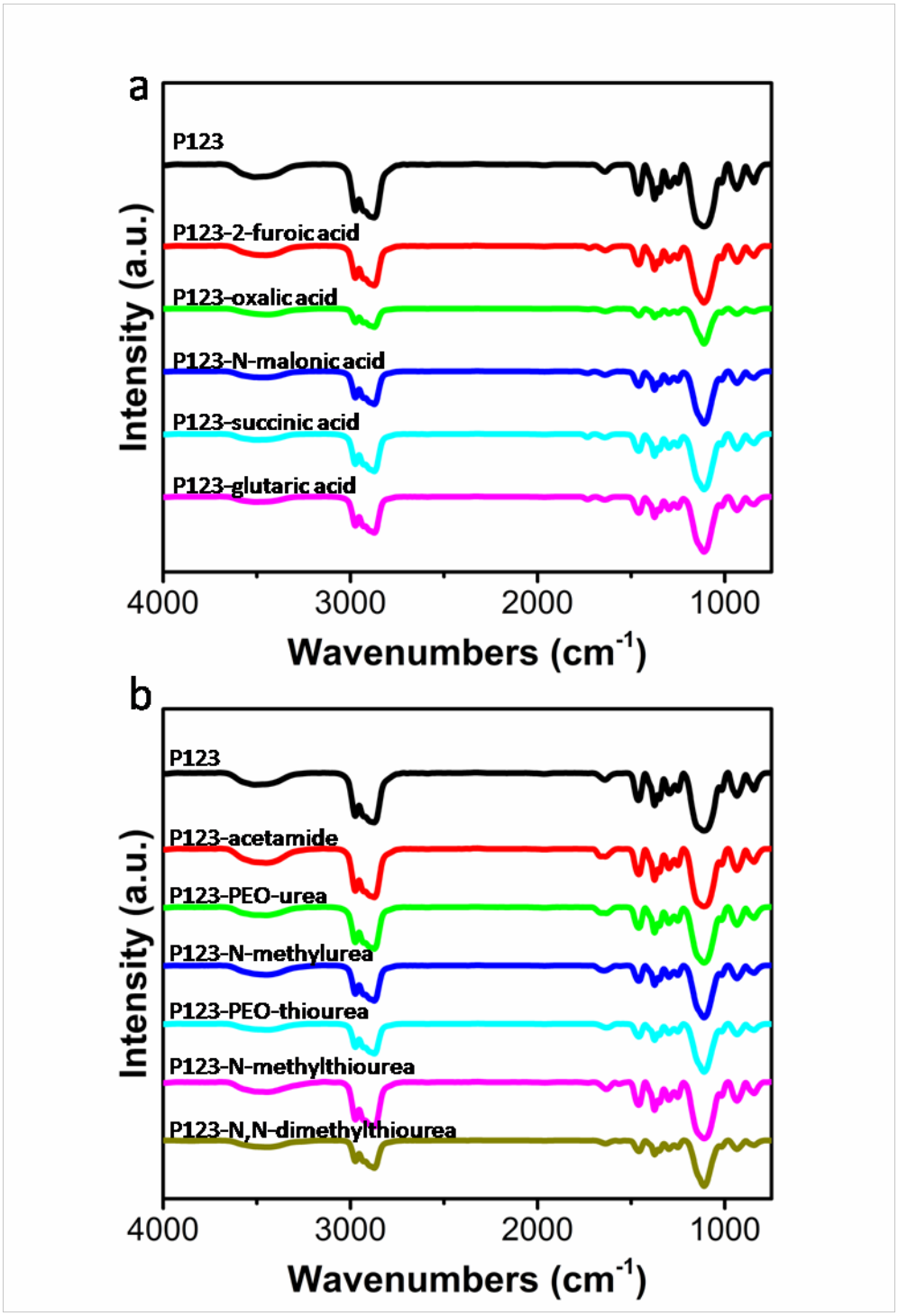

Fig. S2 FTIR spectra of the P123-based PQESs: (a) P123-based PQESs composed by amides-based HBDs including acetamide, urea, N-methylurea, thiourea, N-methylthiourea, and N,N-dimethylthiourea; (b) P123-based PQESs composed by amides-based HBDs including 2-furoic acid, oxalic acid, malonic acid, succinic acid, and glutaric acid.

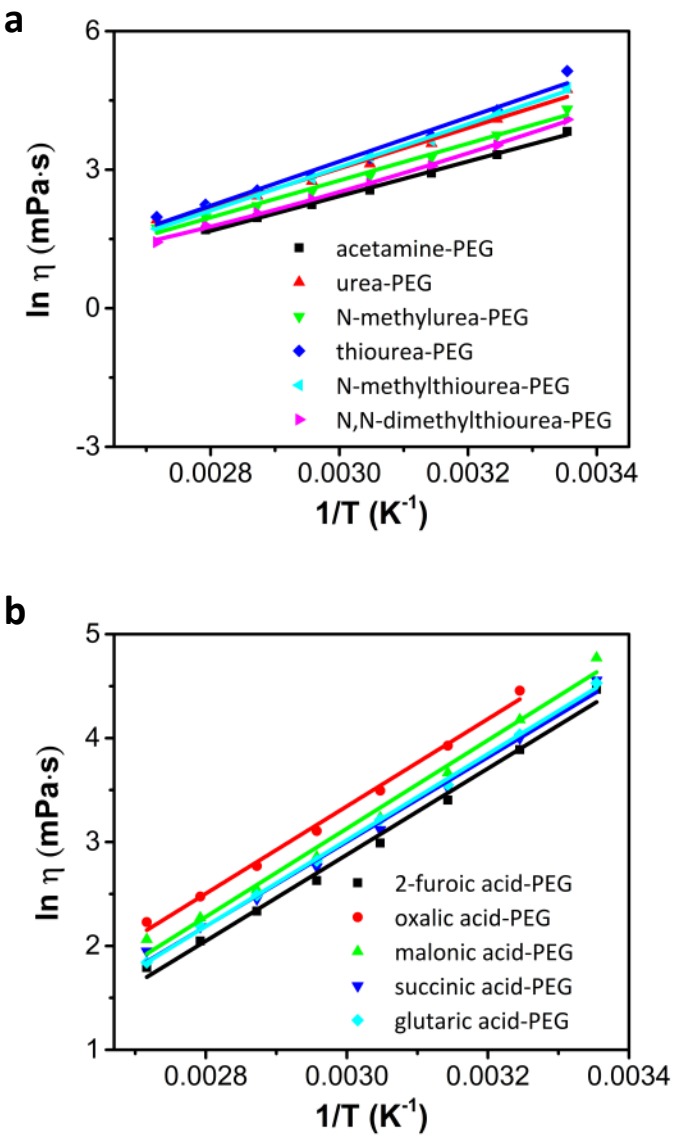

Fig. S3 Plot of ln viscosity vs. reciprocal of temperature for a variety of PQESs: (a) amides-based HBDs including acetamide, urea, N-methylurea, thiourea, N-methylthiourea, and N,N-dimethylthiourea; (b) carboxylic acid-based HBDs including 2-furoic acid, oxalic acid, malonic acid, succinic acid, and glutaric acid.

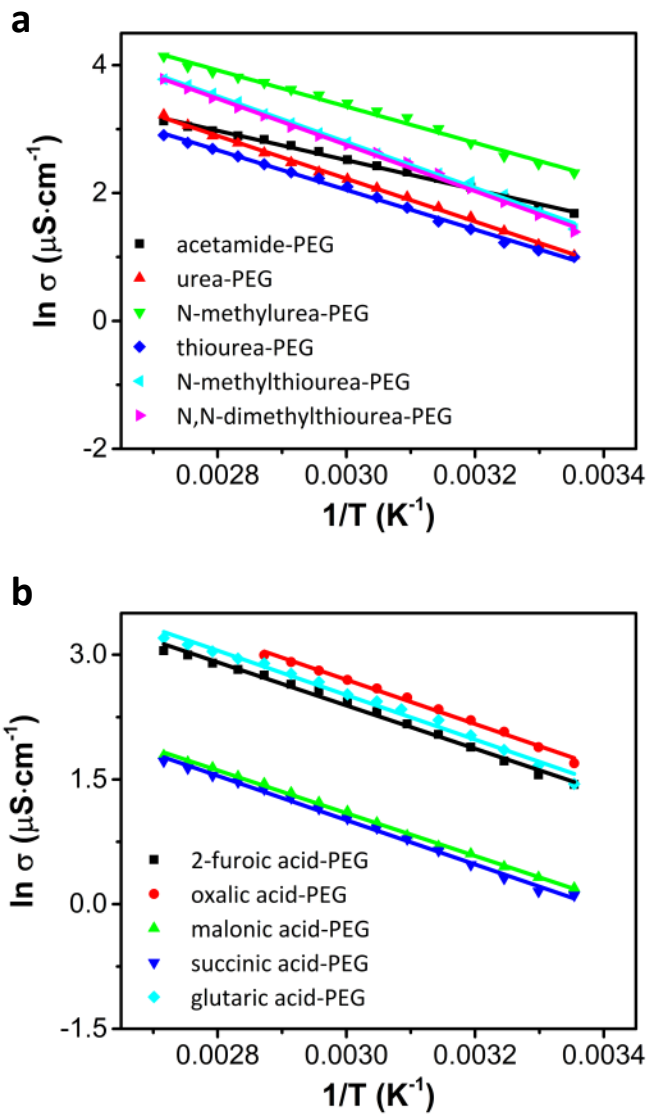

Fig. S4 Plot of ln conductivity vs. reciprocal of temperature for a variety of PQESs: (a) amides-based HBDs including acetamide, urea, N-methylurea, thiourea, N-methylthiourea, and N,N-dimethylthiourea; (b) carboxylic acid-based HBDs including 2-furoic acid, oxalic acid, malonic acid, succinic acid, and glutaric acid.

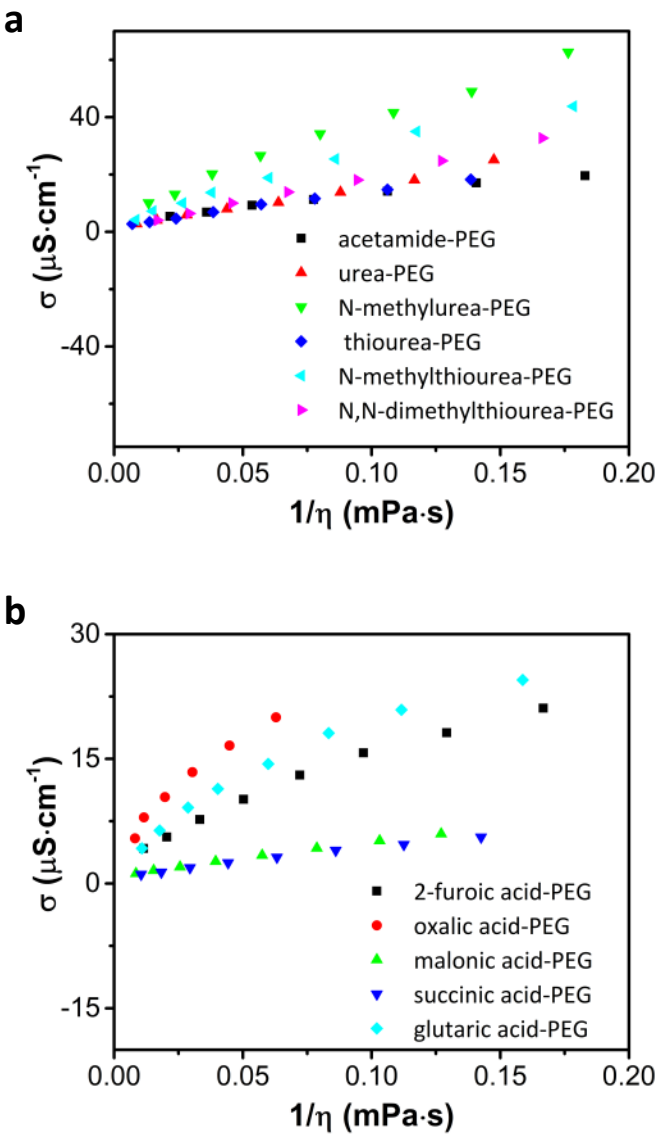

Fig. S5 Plot of conductivity vs. reciprocal of viscosity for a variety of PQESs: (a) amides-based HBDs including acetamide, urea, N-methylurea, thiourea, N-methylthiourea, and N,N-dimethylthiourea; (b) carboxylic acid-based HBDs including 2-furoic acid, oxalic acid, malonic acid, succinic acid, and glutaric acid.

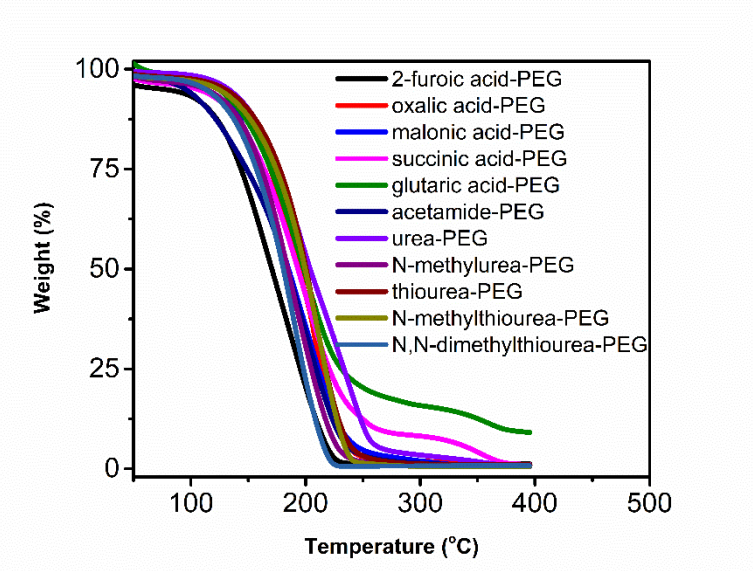

Fig. S6 The thermal stability of the prepared PEG-based PQESs.

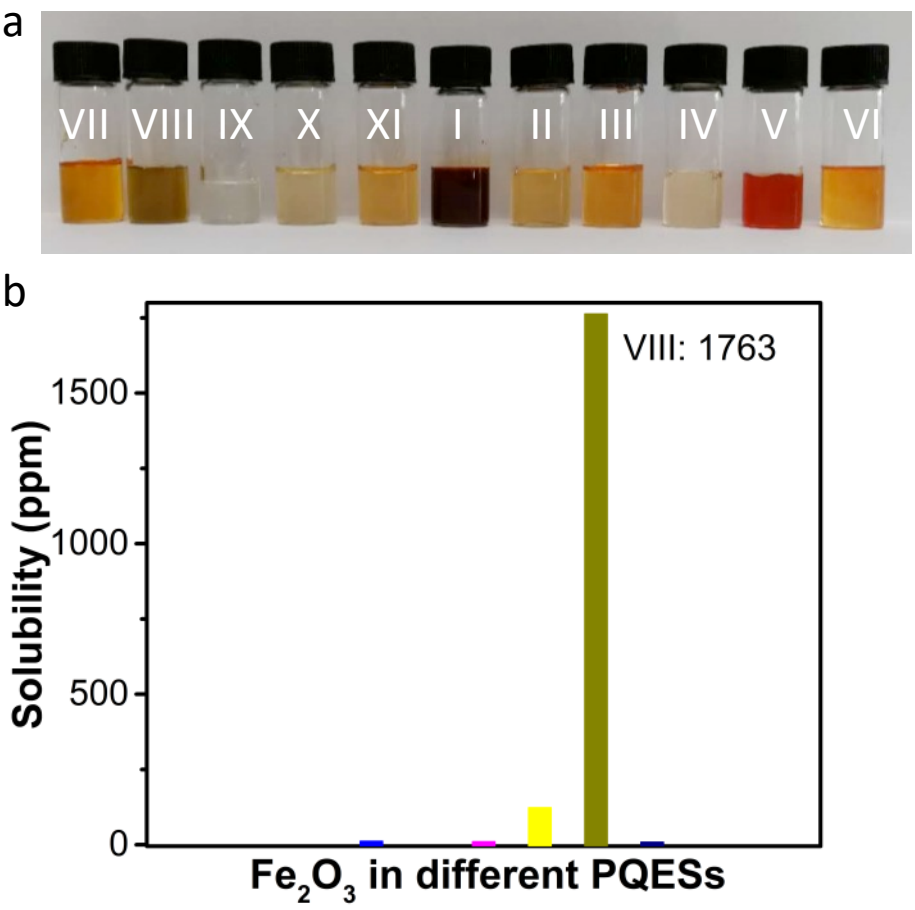

Fig. S7 The dissoving of Fe_2O_3 in the synthesized PQESs: (a) Photographs of PQESs after dissolving Fe_2O_3; (b) solubility of Fe_2O_3 in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

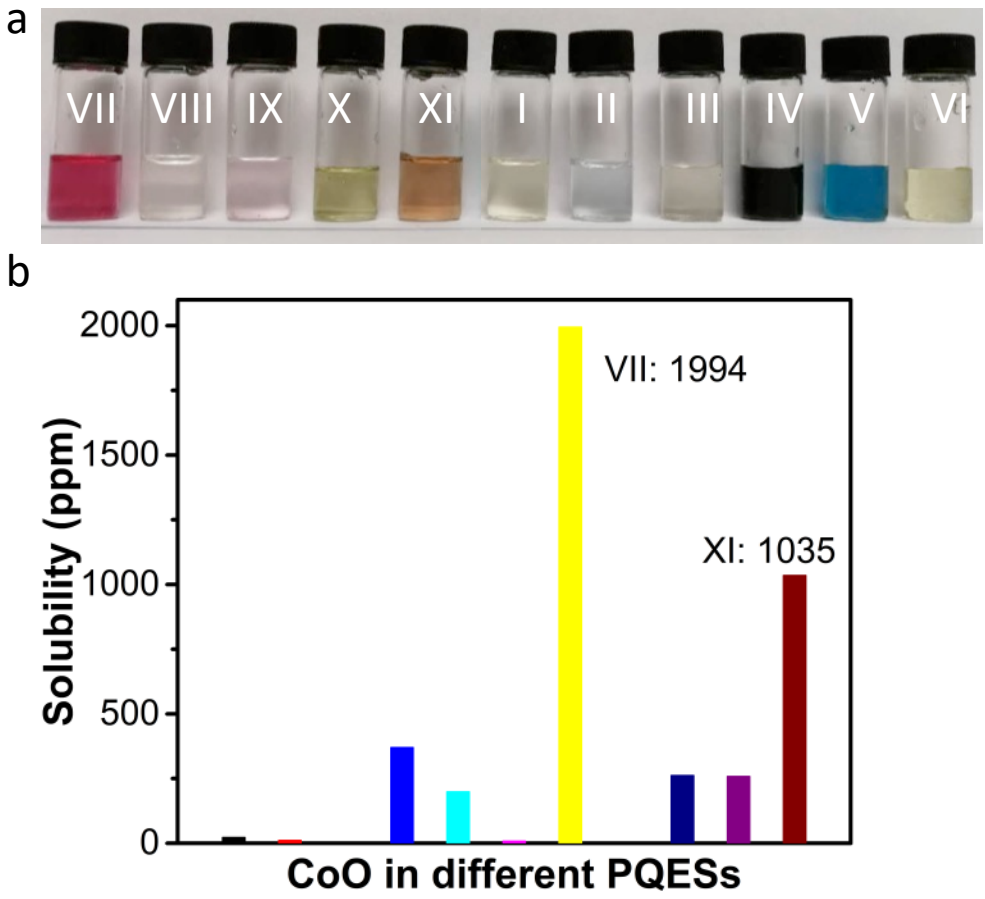

Fig. S8 The dissoving of CoO in the synthesized PQESs: (a) Photographs of PQESs after dissolving CoO; (b) solubility of CoO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

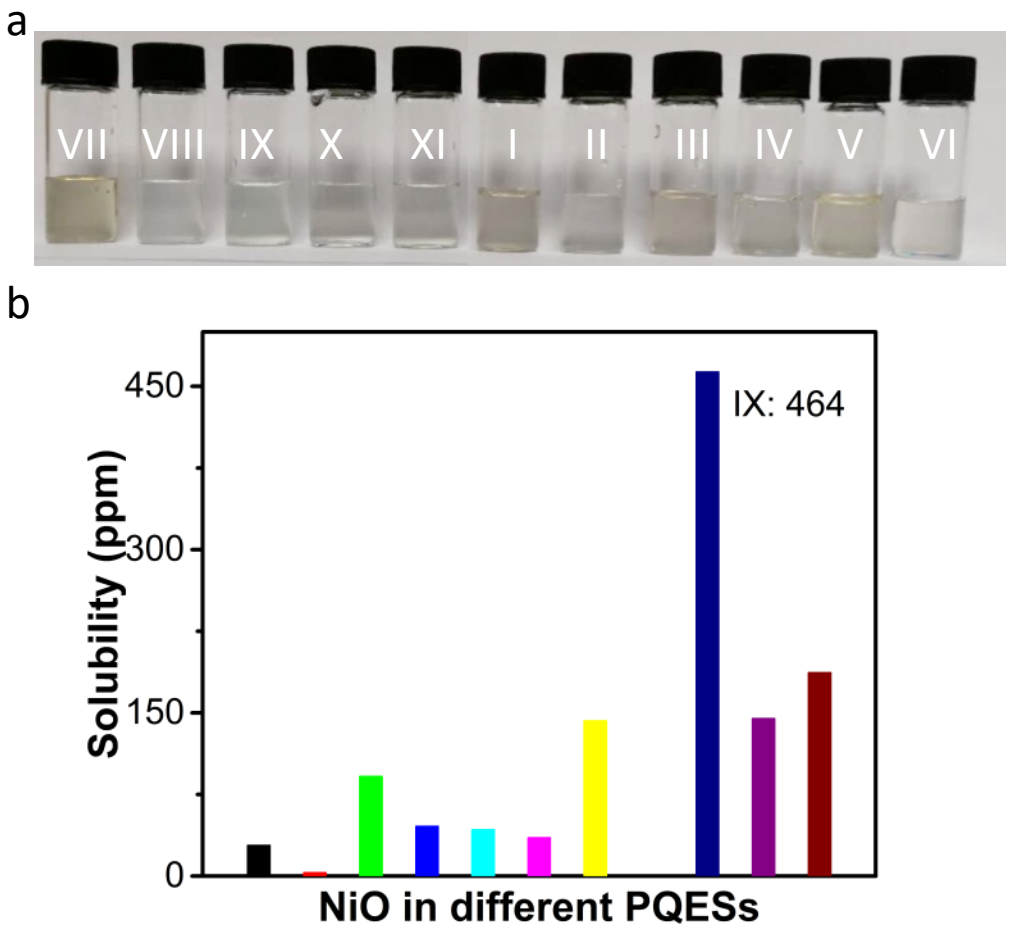

Fig. S9 The dissoving of NiO in the synthesized PQESs: (a) Photographs of PQESs after dissolving NiO; (b) solubility of NiO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

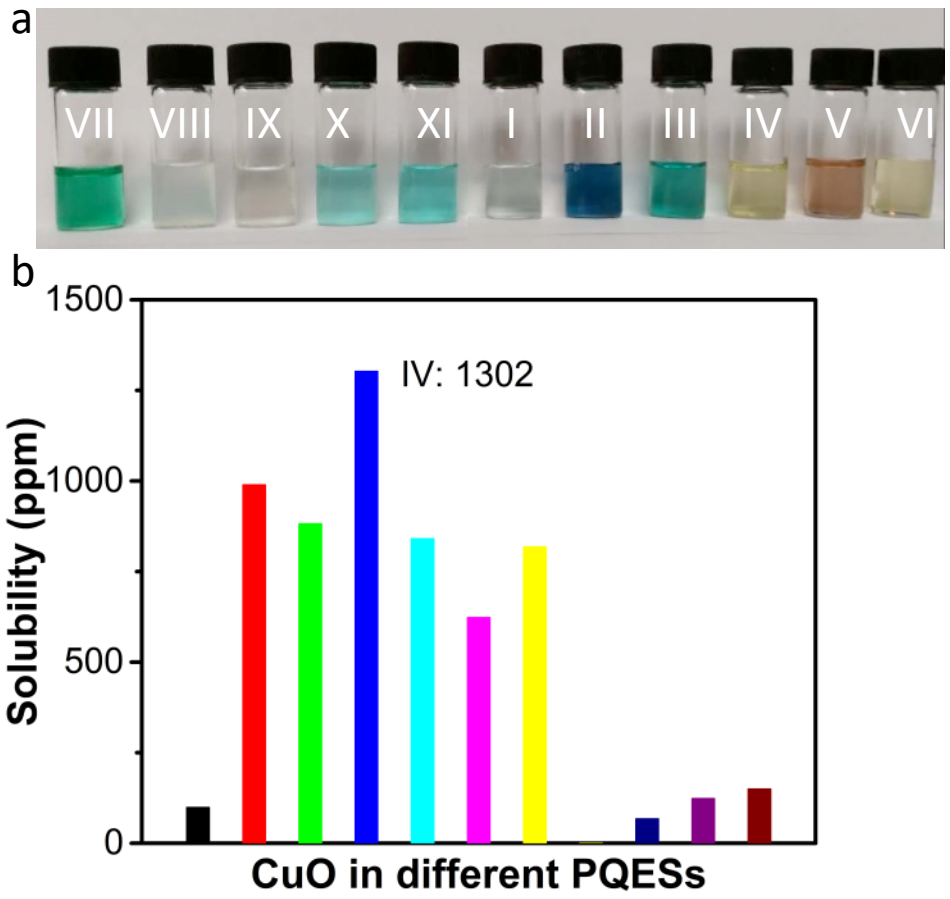

Fig. S10 The dissoving of CuO in the synthesized PQESs: (a) Photographs of PQESs after dissolving CuO; (b) solubility of CuO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

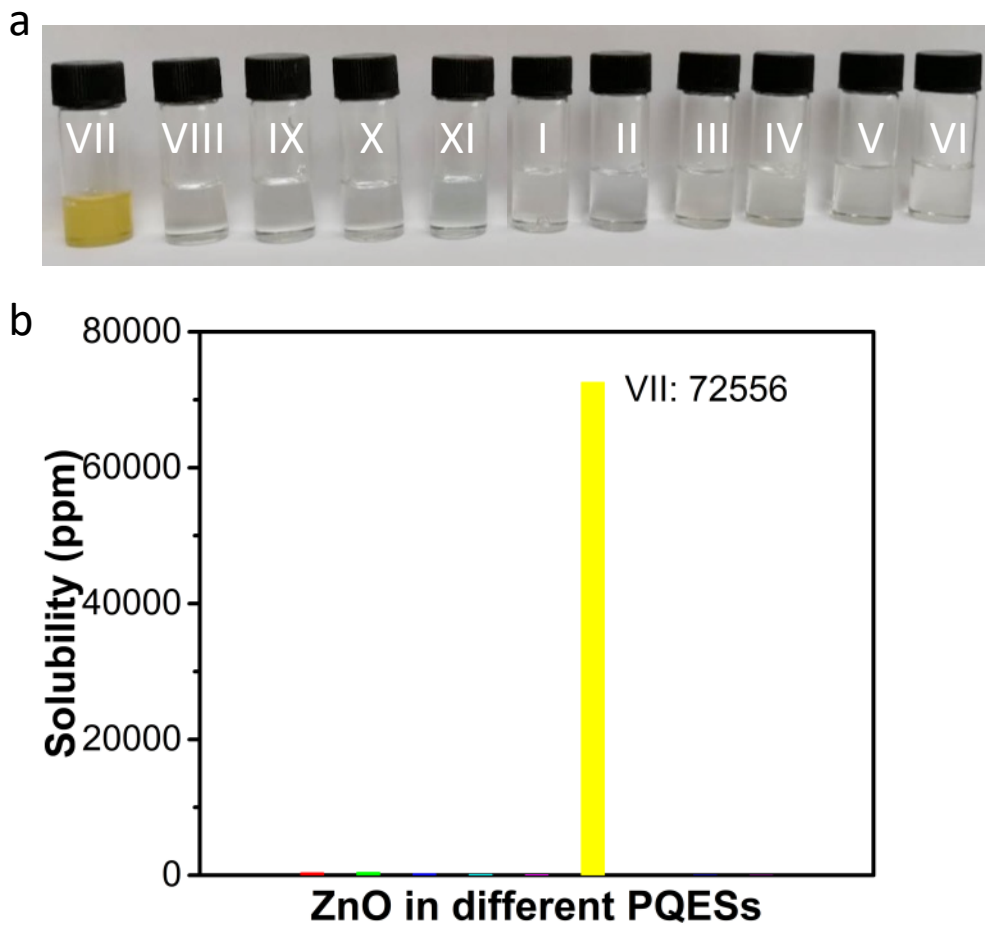

Fig. S11 The dissoving of ZnO in the synthesized PQESs: (a) Photographs of PQESs after dissolving ZnO; (b) solubility of ZnO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

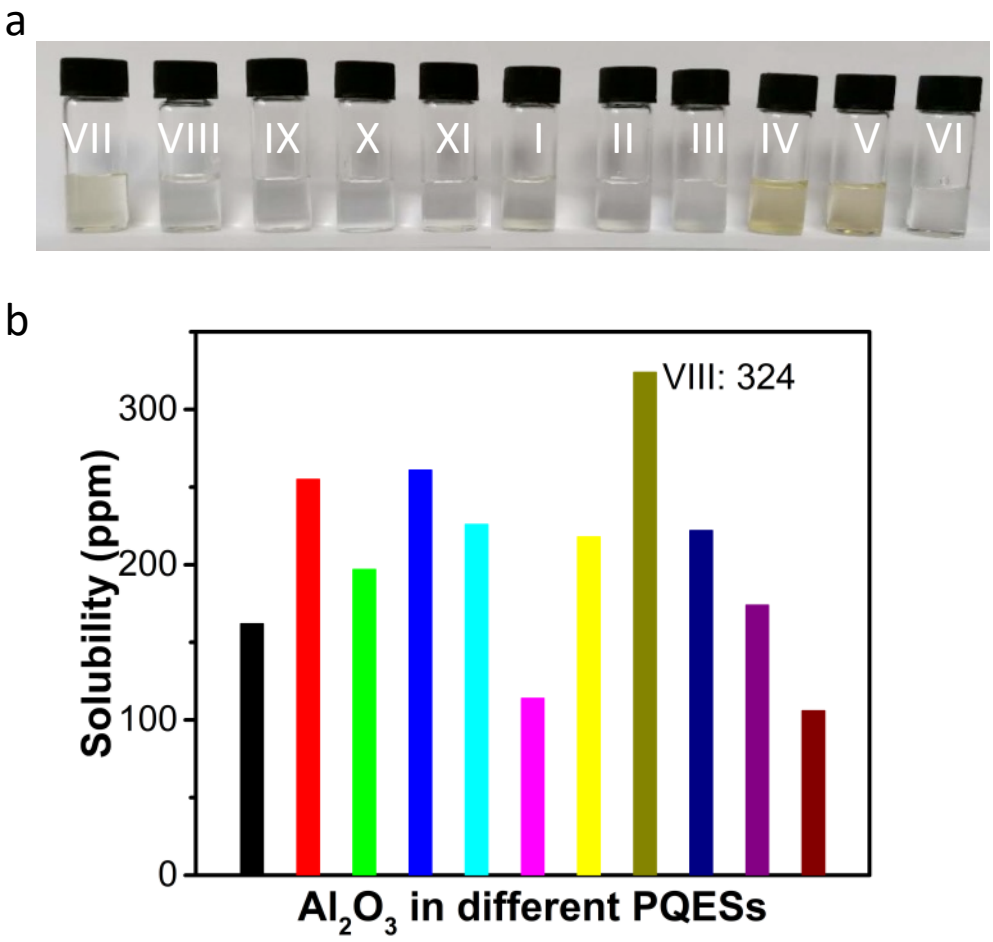

Fig. S12 The dissoving of Al_2O_3 in the synthesized PQESs: (a) Photographs of PQESs after dissolving Al_2O_3; (b) solubility of Al_2O_3 in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

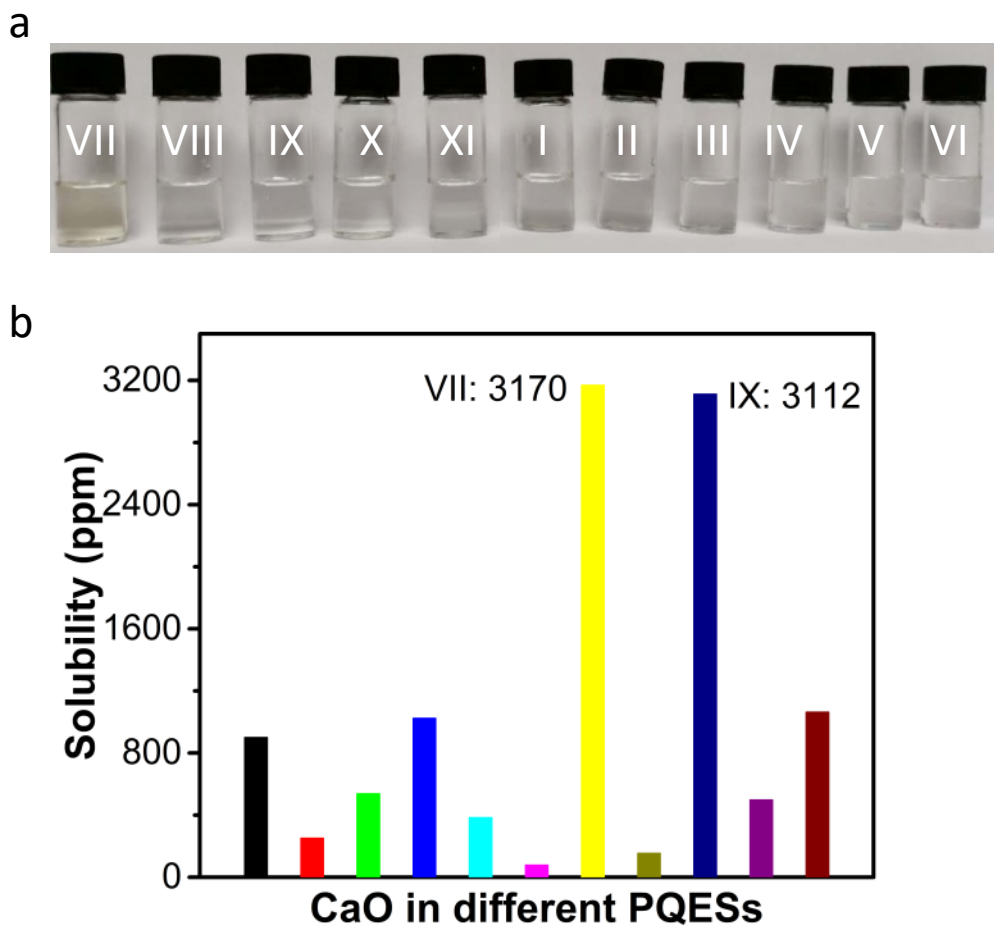

Fig. S13 The dissoving of CaO in the synthesized PQESs: (a) Photographs of PQESs after dissolving CaO; (b) solubility of CaO in differnet PQESs. The HBDs were were composed by acetamide (I), urea (II), N-methylurea (III), thiourea (IV), N-methylthiourea (V), and N,N-dimethylthiourea (VI), 2-furoic acid (VII), oxalic acid (VIII), malonic acid (IX), succinic acid (X), and glutaric acid (XI).

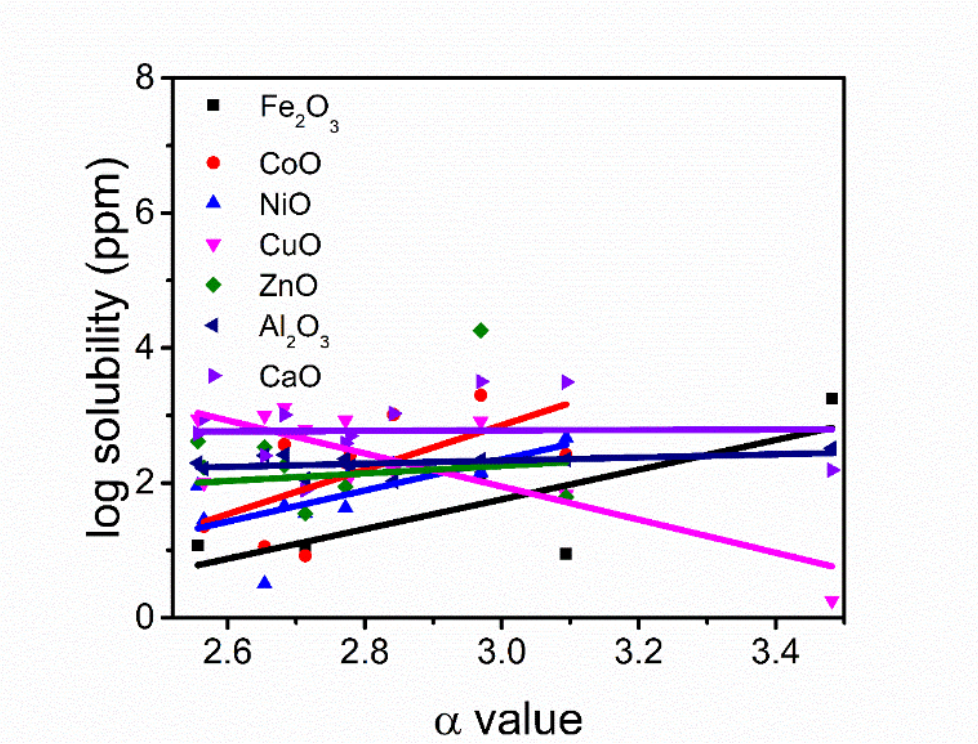

Fig. S14 Relationship of metal oxides (Fe_2O_3, CoO, NiO, CuO, ZnO, Al_2O_3, and CaO) solubility vs α value for PEG-based PQESs. The lines are the linear fitting results of the solubility vs α value.

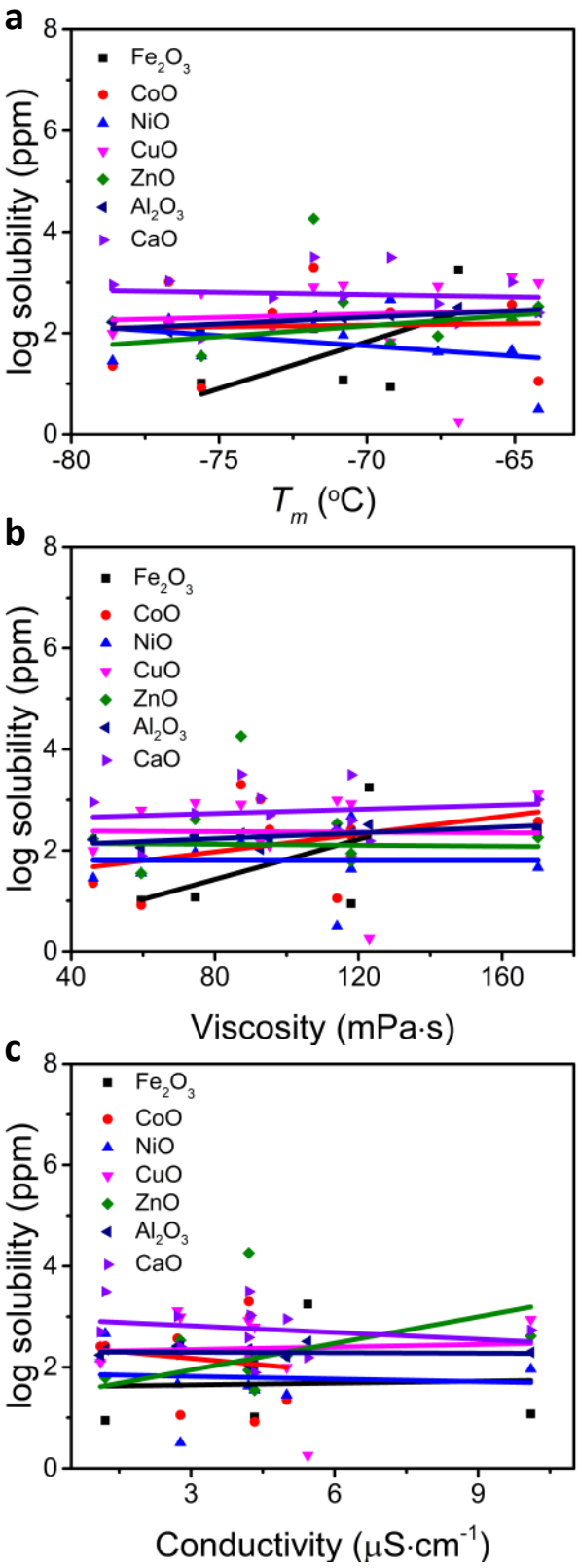

Fig. S15 Relationship of metal oxides (Fe_2O_3, CoO, NiO, CuO, ZnO, Al_2O_3, and CaO) solubility vs T_m (a), viscosity (b), and conductivity (c) values for PEG-based PQESs. The lines are the linear fitting results of the solubility vs T_m (a), viscosity (b), and conductivity (c) values.

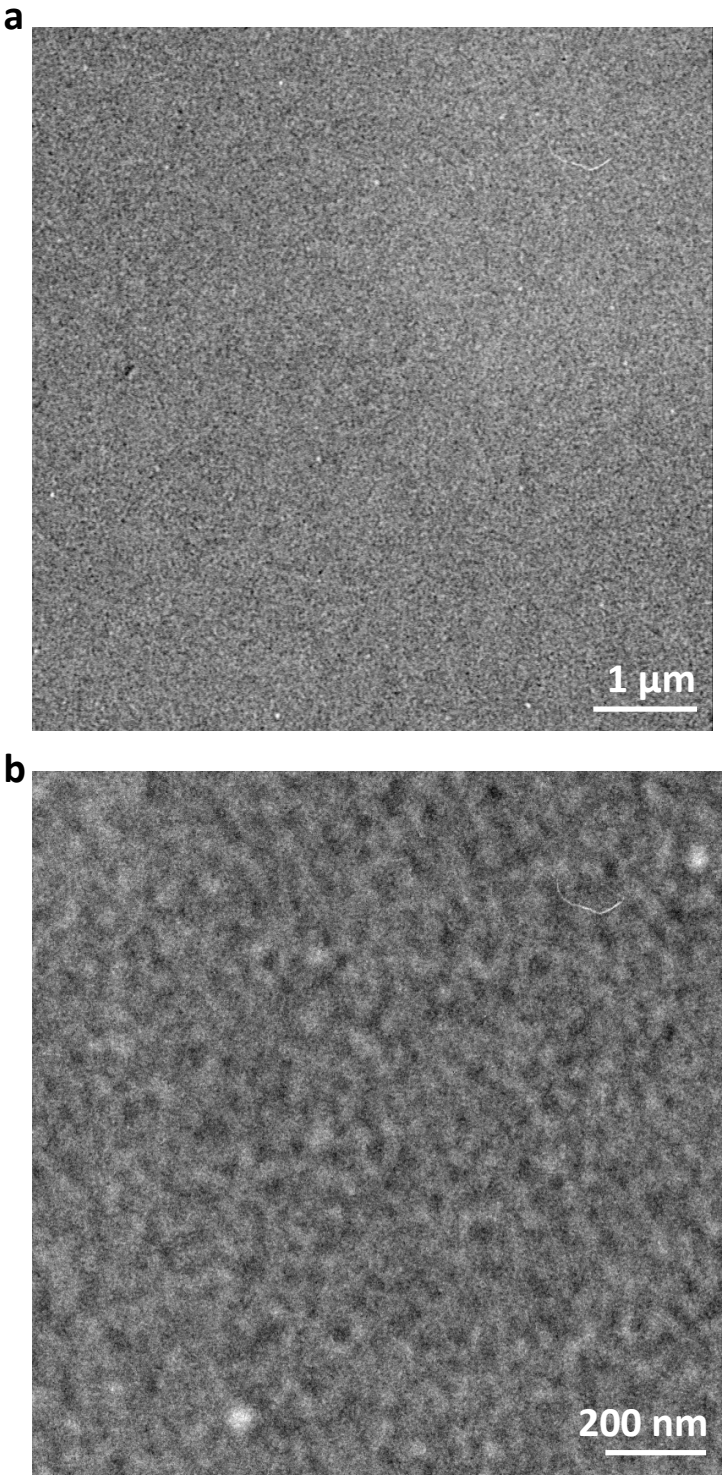

Fig. 16 TEM images of ZnO dissolved in 2-furonic acid-PEG at low (a) and high (b) magnification.

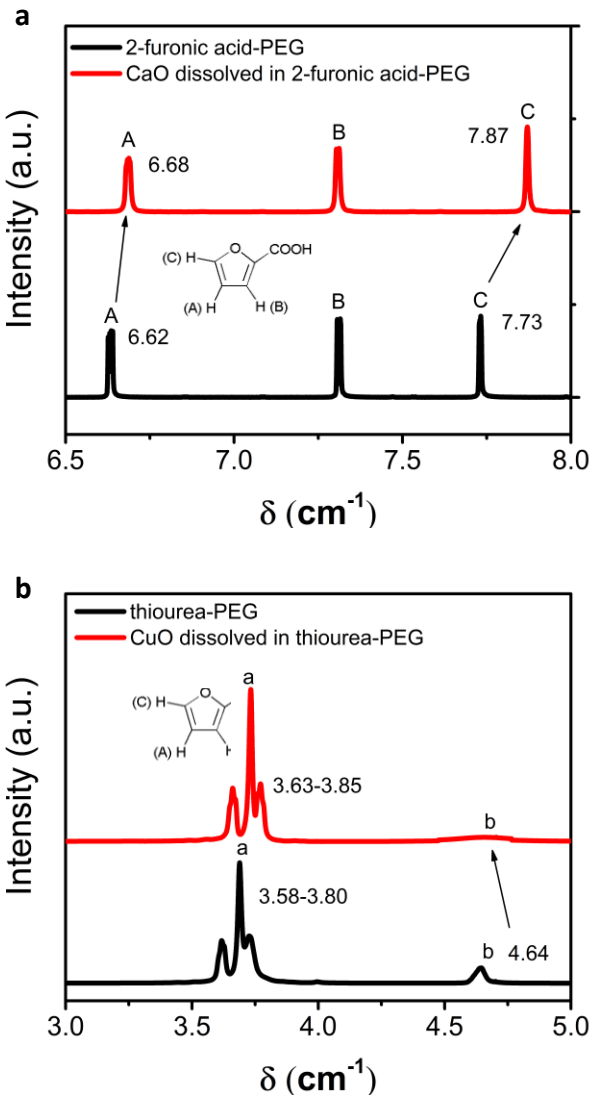

Fig. S17 ^{1}H NMR spectra of before (black) and after (red) metal oxides dissolved in the synthesized PQESs: (a) CaO in 2-furoic acid-PEG and (b) CuO in thiourea-PEG.

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