

## On the effect of ion pairing of Keggin type polyanions with quaternary ammonium cations on redox potentials in organic solvents

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### Electronic Supplemental Information

#### Syntheses

##### **(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NCIO<sub>4</sub>**

A 50 mL ethanol solution containing (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NBr (9.76 g, 17.8 mmol) and 5 mL of a 6 M(aqueous) NaClO<sub>4</sub> water solution (6 M) were mixed with stirring. Water was added to precipitate (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NCIO<sub>4</sub> that was collected as a white solid by filtration. This ion exchange process was repeated twice. The combined white solids were crystallized from hot mixture of water and ethanol, offering colorless plate-like crystals, which were dried under vacuum at 90 °C for 5h. Yield was 8.90g, 88.5%. Anal. Calcd. for C<sub>32</sub>H<sub>68</sub>NCIO<sub>4</sub>: C, 67.86; H, 12.10; N, 2.47; Found: C, 68.48; H, 11.44; N, 2.01. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.27 – 3.12 (m, 8H), 1.63 (br, 8H), 1.43 – 1.19 (m, 40H), 0.88 (t, *J* = 6.8 Hz, 12H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 59.07, 31.76, 29.15, 29.12, 26.40, 22.72, 22.12, 14.19.

##### **(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>NCIO<sub>4</sub>**

(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>NCl (21.32 g, 52.7 mmol) was dissolved in 100 mL toluene and 10 mL of a 4.6 M(aqueous) NaClO<sub>4</sub> solution was added. The mixture was stirred vigorously for 10 min and the water layer was removed. This treatment was repeated twice. The combined organic layers were washed with water three times. Toluene was removed by rotary evaporation, offering a yellow solid. The solid was crystallized from toluene, and dried under vacuum at 80 °C for 5h, the product was obtained as light yellow (14.02 g, 56.9%). Anal. Calcd. for C<sub>32</sub>H<sub>54</sub>NCIO<sub>4</sub>: C, 64.14; H, 11.63; N, 2.99; Found: C, 64.69; H, 11.90; N, 2.52. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.32 – 3.20 (m, 6H), 3.11 (s, 3H), 1.75 – 1.62 (m, 6H), 1.45-1.18 (m, 30H), 0.87 (t, *J* = 6.5 Hz, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 62.04, 48.86, 31.87, 29.28, 29.24, 26.48, 22.81, 22.56, 14.28.

##### **(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NPF<sub>6</sub>**

A 4 mL dichloromethane solution of (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NBr (0.20g, 0.37 mmol) was mixed with 2 mL of a 1 M (aqueous) NH<sub>4</sub>PF<sub>6</sub> solution.. The mixture was stirred vigorously for 10 min, the water layer was removed, and this treatment was repeated twice. The organic layer was washed with water three times, dichloromethane was removed by evaporation and the light yellow solid was dried under vacuum at 80 °C for 3h (0.16 g, 71.4%). Anal. Calcd. for C<sub>32</sub>H<sub>68</sub>NPF<sub>6</sub>: C, 62.82; H, 11.20; N, 2.29; Found: C, 62.99; H, 11.35; N, 1.70. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.18 - 3.08 (m, 8H), 1.60 (m, 8H), 1.42-1.38 (m, 40H), 0.88 (t, *J* = 6.8 Hz, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): 59.05, 31.84, 29.20, 26.42, 22.81, 22.10, 14.28. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): -143.87 (m, *J*<sub>P-F</sub> = 712.8 Hz). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ 89.27 (d, *J*<sub>F-P</sub> = 712.8 Hz).

##### **(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>NPF<sub>6</sub>**

The compound was prepared from (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>NCl by the same method as (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NPF<sub>6</sub>.  
Anal. Calcd. for C<sub>25</sub>H<sub>54</sub>NPF<sub>6</sub>: C, 58.46; H, 10.60; N, 2.73; Found: C, 59.01; H, 10.80; N, 2.25. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>): 3.17 (m, 6H), 3.00 (s, 3H), 1.64 (m, 6H), 1.44 – 1.19 (m, 30H), 0.88 (t, *J* = 6.8 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): 61.90, 48.56, 31.75, 29.12, 29.11, 26.29, 22.70, 22.34, 14.17. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): -143.83 (m, *J*<sub>P-F</sub> = 712.7 Hz). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): 89.72 (d, *J*<sub>F-P</sub> = 712.7 Hz)

#### **[(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>**

A 3 mL water solution of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O (0.20 g) and a 2 mL dichloromethane solution of (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NBr (68 mg, 0.12 mmol, *ca.*0.6 eqv.) were mixed and stirred vigorously for 5 min. The organic layer was washed with water several times until the water layer become neutral using a pH indicator. Dichloromethane was removed by evaporation. The colorless solid was dried under vacuum at 80 °C for 3h.

TGA, cation content exptl. 33.6%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N)<sub>2</sub>O 33.3%. IR (cm<sup>-1</sup>): 2955, 2927, 2872, 2853, 1484, 1467, 1377, 1080, 985, 977, 896, 817.

#### **[(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>**

The compound was prepared from H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O and (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>NCl by the same method as [(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

TGA, cation content exptl. 28.6%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N)<sub>2</sub>O 28.3%. IR (cm<sup>-1</sup>): 3040, 2953, 2926, 2869, 2856, 1482, 1466, 1377, 1079, 989, 980, 895, 816,

#### **[(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>**

The compound was prepared from H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O by the same method as [(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

TGA, cation content exptl. 39.9%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N)<sub>2</sub>O 40.0%. IR (cm<sup>-1</sup>): 2954, 2925, 2869, 2855, 1482, 1466, 1377, 1011, 970, 919, 883, 798.

#### **[(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N]<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>**

The compound was prepared from H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O by the same method as [(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

TGA, cation content exptl. 34.6%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N)<sub>2</sub>O 34.4%. IR (cm<sup>-1</sup>): 3038, 2954, 2926, 2868, 2855, 1467, 1377, 1009, 968, 919, 882, 800.

**K<sub>5</sub>BW<sub>12</sub>O<sub>40</sub>·11H<sub>2</sub>O** was prepared according to Copaux's method as modified in the literature (C. Rocchiccioli-Deltcheff; M. Fournier; R. Franck; R. Thouvenot. *Inorg. Chem.* 1983, **22**, 207.

#### **[(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>5</sub>BW<sub>12</sub>O<sub>40</sub>**

K<sub>5</sub>BW<sub>12</sub>O<sub>40</sub>·11H<sub>2</sub>O (0.30 g, 92 umol) was dissolved in 3 mL water (pH~8, adjusted by NaHCO<sub>3</sub> before the polyoxometalate was added). Then a 2 mL dichloromethane solution of (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NBr (0.15 g, 0.28 mmol, 0.6 eqv.) was added. The mixture was stirred vigorously for 5 min, and the organic layer was washed with water (pH~8, adjusted by NaHCO<sub>3</sub>) two times. Dichloromethane was removed by evaporation. The colorless solid was dried under vacuum at 80 °C for 3h.

TGA, cation content exptl 45.7%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N)<sub>2</sub>O 45.7%. IR (cm<sup>-1</sup>): 2954, 2926, 2868, 2855, 1482, 1468, 1378, 994, 953, 903, 824.

**[(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N]<sub>5</sub>BW<sub>12</sub>O<sub>40</sub>**

The compound was prepared in the same way as [(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>5</sub>BW<sub>12</sub>O<sub>40</sub> from K<sub>5</sub>BW<sub>12</sub>O<sub>40</sub>·11H<sub>2</sub>O. TGA, cation content exptl 39.8%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N)<sub>2</sub>O 40.0%. IR (cm<sup>-1</sup>): 3039, 2955, 2925, 2868, 2855, 1483, 1467, 1378, 991, 949, 898, 822.

**K<sub>4</sub>PVW<sub>11</sub>O<sub>40</sub>·2H<sub>2</sub>O** was prepared from H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, according to the published method (P. J. Domaille. *J. Am. Chem. Soc.* 1984, **106**, 7677.)

**[(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>4</sub>PVW<sub>11</sub>O<sub>40</sub>**

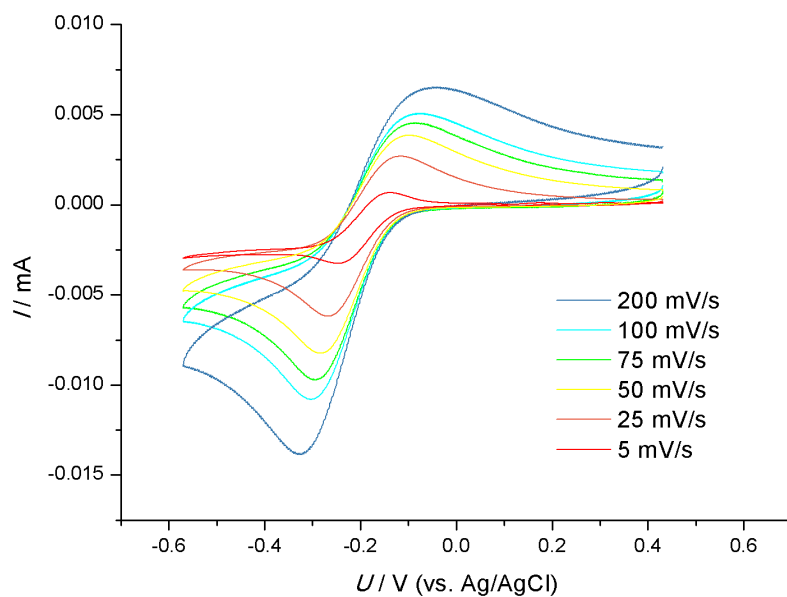
The compound was prepared from K<sub>4</sub>PVW<sub>11</sub>O<sub>40</sub>·2H<sub>2</sub>O by the same method as [(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

TGA, cation content exptl 41.0%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N)<sub>2</sub>O 41.2%. IR (cm<sup>-1</sup>): 2954, 2926, 2868, 2855, 1482, 1466, 1378, 1094, 1067, 962, 887, 808, 519.

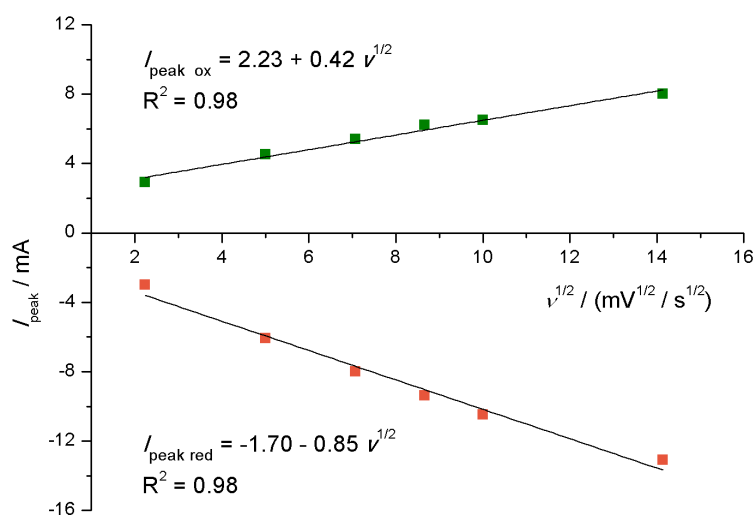
**[(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N]<sub>4</sub>PVW<sub>11</sub>O<sub>40</sub>**

The compound was prepared from K<sub>4</sub>PVW<sub>11</sub>O<sub>40</sub>·2H<sub>2</sub>O by the same method as [(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>N]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

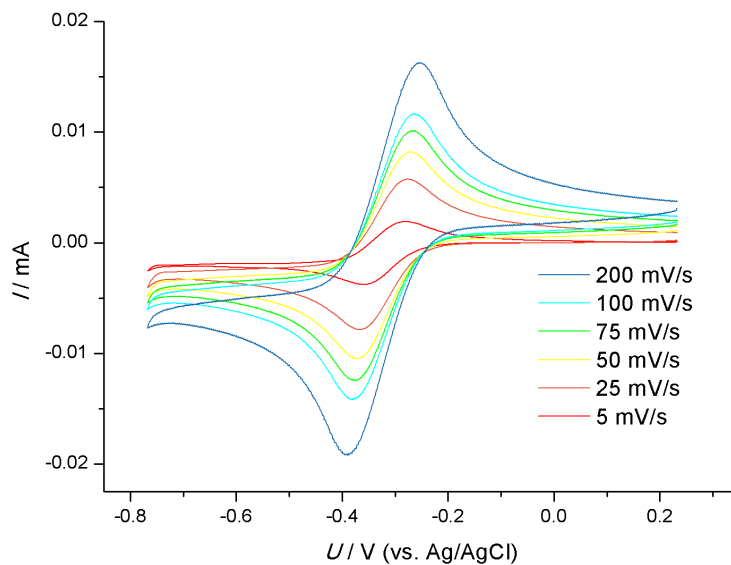
TGA, cation content exptl 35.0%, calcd for ((C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N)<sub>2</sub>O 35.7%. IR (cm<sup>-1</sup>): 3041, 2956, 2924, 2871, 2857, 1483, 1467, 1376, 1094, 1068, 955, 888, 808, 519.



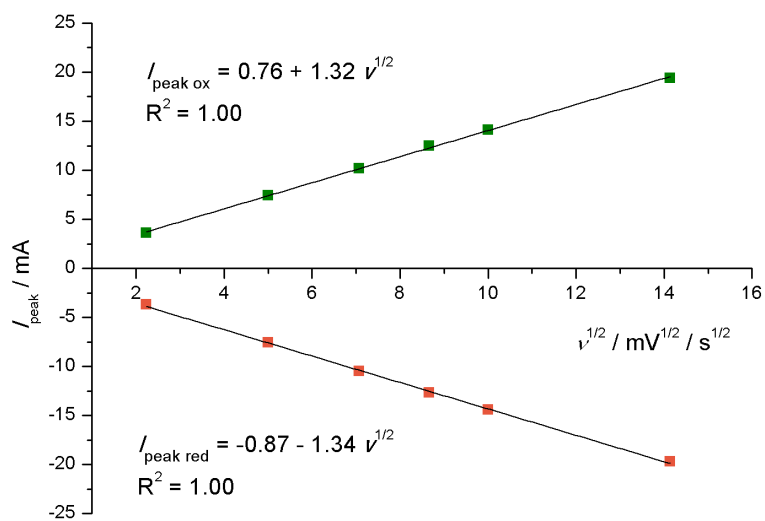
**Figure S1.** Cyclic voltammetry scans of 2mM C83-PW<sub>12</sub>O<sub>40</sub> in dichloromethane at scanning rates ranging from 5 mV/s to 200 mV/s. Electrolyte 0.1 M (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH<sub>3</sub>NClO<sub>4</sub>; Ar, 20 °C; Pt working electrode; Ag/AgCl in 3.0 M KCl water solution reference electrode; counter electrode - Pt wire.



**Figure S2.** The dependence of oxidation and reducing peak current of C83-PW<sub>12</sub>O<sub>40</sub> on the square root of scan rate.



**Figure S3.** Cyclic voltammetry scans of C84-PW<sub>12</sub>O<sub>40</sub> in dichloromethane at scanning rates ranging from 5 mV/s to 200 mV/s. Electrolyte 0.1 M (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>NClO<sub>4</sub>; Ar, 20 °C; Pt working electrode; Ag/AgCl in 3.0 M KCl water solution reference electrode; counter electrode - Pt wire.



**Figure 4s.** The dependence of oxidation and reducing peak current of C84-PW<sub>12</sub>O<sub>40</sub> on the square root of scan rate.

**Table S1.** The reduction/oxidation potentials of C83-PW<sub>12</sub>O<sub>40</sub> and C84-PW<sub>12</sub>O<sub>40</sub> in dichloromethane at scanning rate from 5 mV/s to 200 mV/s in dichloromethane solution.

Scanning rate	C83-PW <sub>12</sub> O <sub>40</sub>			C84-PW <sub>12</sub> O <sub>40</sub>		
	$E_{\text{red}}$	$E_{\text{ox}}$	$E_{1/2}$	$E_{\text{red}}$	$E_{\text{ox}}$	$E_{1/2}$
5mV/s	-0.248	-0.139	-0.194	-0.360	-0.281	-0.321
25 mV/s	-0.267	-0.117	-0.192	-0.367	-0.276	-0.322
50 mV/s	-0.281	-0.097	-0.189	-0.371	-0.271	-0.321
75 mV/s	-0.294	-0.086	-0.190	-0.376	-0.267	-0.322
100 mV/s	-0.302	-0.078	-0.190	-0.379	-0.264	-0.322
200 mV/s	-0.325	-0.046	-0.186	-0.390	-0.255	-0.323

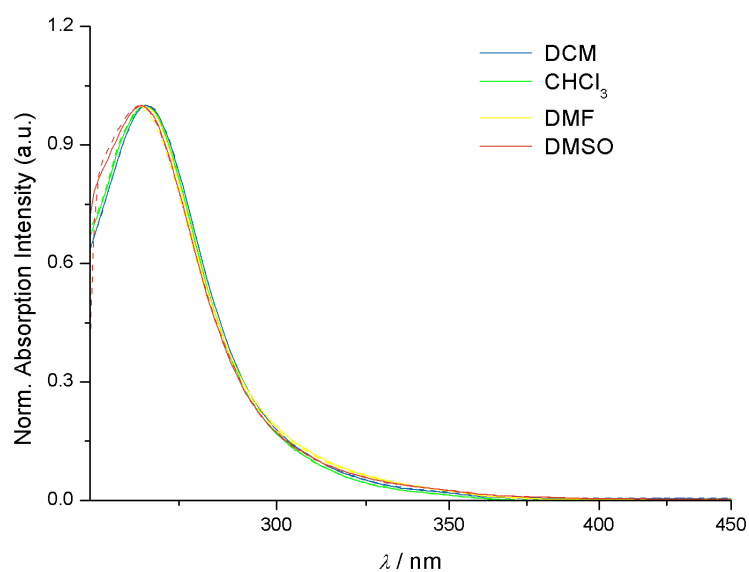
**Table S2.** Dielectric constant<sup>1</sup> and Kamlet-Taft<sup>2</sup> parameter sets.

Solvent	Dielectric constant	Kamlet-Taft parameter		
		$\pi^*$	$\alpha$	$\beta$
Chloroform	4.8	0.58	0.44	0
Dichloromethane	8.9	0.82	0.30	0
Pyridine	12.9	0.87	0	0.64
Cyclohexanone	18.2	0.76	0	0.53
Acetone	20.6	0.71	0.08	0.48
2-nitropropane	25.5	NF	NF	NF
DMF	36.7	0.88	0	0.69
DMSO	46.6	1.00	0	0.76

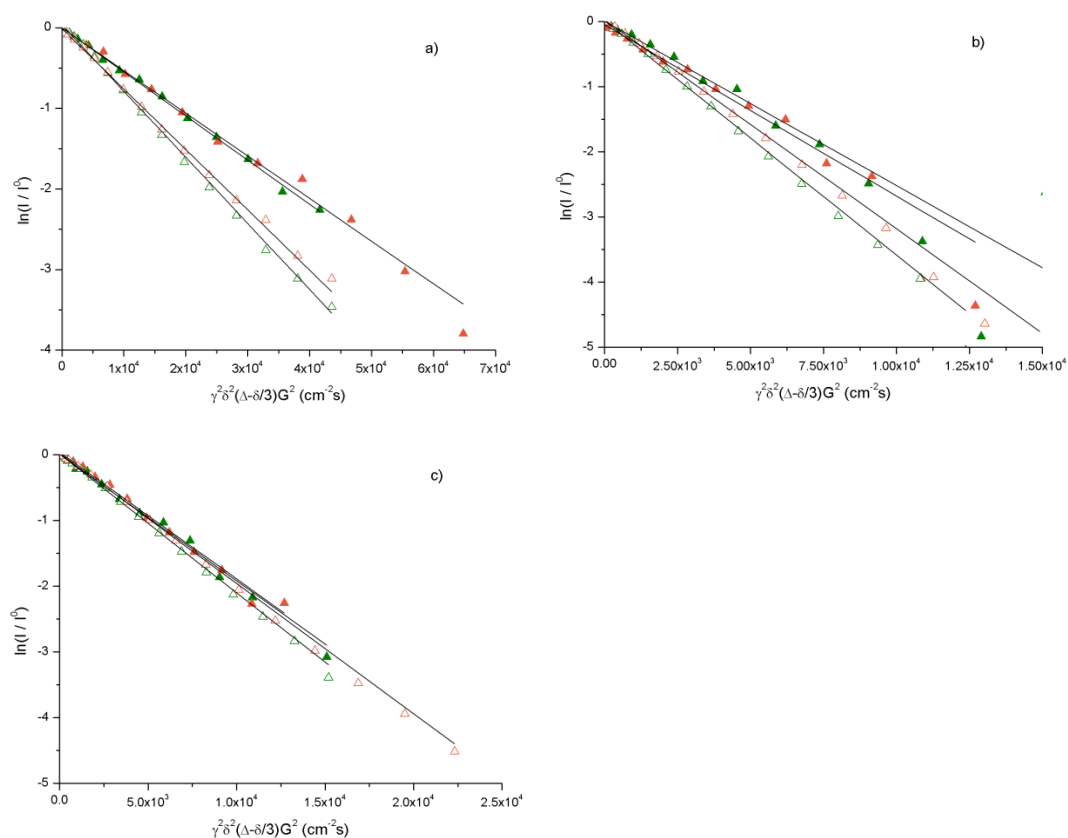
**Table S3.** Viscosity of the deuterated solvents at 25°C.

Solvent	CD <sub>2</sub> Cl <sub>2</sub> <sup>3</sup>	Acetone-d <sub>6</sub> <sup>4</sup>	DMSO-d <sub>6</sub> <sup>4</sup>
Viscosity (cP)	0.417	0.326	1.99

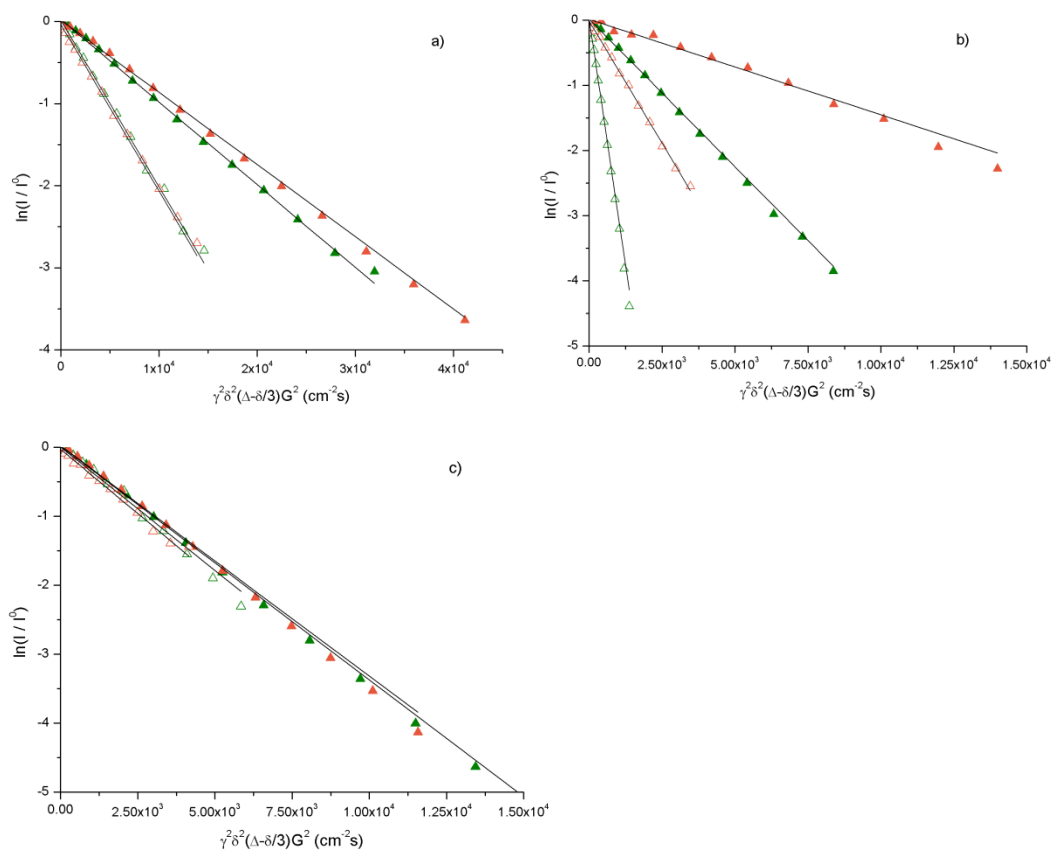
1. Ian M. Smallwood, Handbook of organic solvent properties.
2. Mortimer J. Kamlet, José-Luis M. Abboud, Michael H. Abraham, and R. W. Taft, *J. Org. Chem.* 1983, 48, 2877.
3. Deyu Li, Gerald Kagan, Russell Hopson, Paul G. Williard, *J. Am. Chem. Soc.* 2009, 131, 5627.
4. Manfred Holz, Xi-an Mao, Dieter Seiferling, *J. Chem. Phys.* 1996, 104, 669.



**Figure S5.** UV-Vis absorption spectra in various solvents.  $2 \times 10^{-5}$  M C83-PW<sub>12</sub>O<sub>40</sub> (solid line) and C84-PW<sub>12</sub>O<sub>40</sub> (dashed line)



**Figure S6.** <sup>1</sup>H and <sup>31</sup>P DOSY NMR signal decays of C84-PW<sub>12</sub>O<sub>40</sub> (orange) and C83-PW<sub>12</sub>O<sub>40</sub> (green) in DMSO (a), acetone (b) and dichloromethane solutions (c). The solid triangles refer <sup>1</sup>H signals, and the hollow triangles refer to <sup>31</sup>P signals. The solid line is the linear fitting of the data according to Stejskal-Tanner equation.



**Figure S7.** <sup>1</sup>H and <sup>31</sup>P DOSY NMR signal decays of C84-PF<sub>6</sub> (orange) and C33-PF<sub>6</sub> (green) in DMSO (a), acetone (b), dichloromethane solutions (c). The solid triangles refer <sup>1</sup>H signals, and the hollow triangles refer to <sup>31</sup>P signals. The solid line is the linear fitting of the data according to Stejskal-Tanner equation.