Electronics Supplementary Information

# Chiral and Conductive Viologen-based Supramolecular Gels Exhibiting Tunable Charge-Transfer Properties

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# NMR spectra



Fig. S1 <sup>1</sup>H NMR spectra of 2 (300MHz, CDCl<sub>3</sub>)

Fig. S2  $^1\text{H}$  NMR spectra of  $1(\text{Br})_2$  (300MHz, DMSO-d\_6). 3.33ppm: water, 2.50ppm DMSO



# CENTRE COMMUN DE SPECTROMETRIE DE MASSE

#### Analysis Info

Analysis Name Method	Impact2_230310_ Tune_pos_Standa	15_VA31.d rd.m	Acquisition Date	3/10/2023 4:33:49 PM		
Comment			- 18	Instrument / Ser#	impact II	1825265.1
Acquisition Par	ameter			and the second second		0001
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3	Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heat	er 200	°C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0	Vmin
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Va	lve Sou	rce



Fig. S3 HRMS report of 2, indicated as M on the spectra. Species detected as MNa<sup>+</sup>

## CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name Impact2\_210720\_07\_VA11.d Method Tune\_pos\_Standard.m Comment

Acquisition Date 7/20/2021 2:09:18 PM Instrument/ Ser# impact II 1825265.1

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Acquisition Par	ameter				
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	20 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	1500.0 Vpp	Set Divert Valve	Source



Fig. S4 HRMS report of  $1^{2+}$ , indicated as  $M^{2+}$  on the spectra.

### Rheology



**Fig. S5** Evolution of G' (full square) and G'' (empty circle) as a function of time t as the temperature T (dots) decreases: (a) using a gap set to h=0.5 mm and monitoring F and (c) using a constant force F=0 N and monitoring the gap h.



Fig. S6 Schematic representation of rheological characterization data analysis  $0.2wt\% 1^{2+}$  gel in pentanol [TBAI] = 50mM, [LiTFSI] = 100mM.

In order to determine the gelation temperatures ( $T_g$ ) of the gels, the samples were preheated in the liquid state and introduced in the rheometer thermalized at a temperature at least 10°C above the gel melting temperature.

Evaporation effects could be minimized upon using a solvent trap filled with the same solvent as the one used for gelation. The sol–gel transition was achieved by cooling the sample at a rate of 2°C/min down to a final temperature of 20°C. The loss (*G*") and elastic (*G*') moduli together with the gap distance (*h*) and the normal force *F* were measured as a function of time during the cooling process at a frequency f = 1 Hz and strain amplitude of  $\gamma = 0.1$ %. As shown in Fig. S6,  $T_g$  was obtained by considering the temperature from which the G' > G''.

Gelation temperature measurements have been performed on  $\mathbf{1}(Br)_2$  gels of different ionic compositions. The results are reported in Table S.1 and in Fig. 2 (main text).

For low values of [TFSI<sup>-</sup>]/[I<sup>-</sup>] (resp [TFSI<sup>-</sup>]/[Br<sup>-</sup>]) concentration ratios, typically [TFSI<sup>-</sup>]/[I<sup>-</sup>] < 1 (resp [TFSI<sup>-</sup>]/[Br<sup>-</sup>] < 0.5), the samples were able to form gels but exhibited higher  $T_g$  (causing problem of solvent evaporation) associated with quicker gelation (making the sample contraction more violent upon gelation). For these reasons the  $T_g$  could not be measured using the previously described protocol.

For high values of  $[TFSI^-]/[I^-]$  (resp  $[TFSI^-]/[Br^-]$ ) concentration ratios, typically  $[TFSI^-]/[I^-] \ge 4$  (resp  $[TFSI^-]/[Br^-] \ge 2$ ), the samples were not able to form gels. Upon cooling in the rheometer several millimeters large aggregates were formed (similar to those observed in absorbance spectroscopy experiment, see Fig. S14). The formation of such aggregates could be detected by an increase in *G'* reaching values around 100Pa respectively at T = 20 °C for  $[TFSI^-]/[I^-]=4$  and T = 55°C for  $[TFSI^-]/[Br^-] = 2.5$ . (see Fig. S9)

Table S1 Evolution of gelation	temperature for gels of	different ionic compositions	([1(Br) <sub>2</sub> ] = 1.3 mM in	pentanol for al samples).
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Composition	# samples	Measured T <sub>g</sub> (°C)	Average of $T_{g}$	Standard deviation
			(°C)	of I <sub>g</sub> (°C)
100 mM LiTFSI, 100 mM	4	77, 85, 72, 85	79.8	5.6
ТВАІ				
100 mM LiTFSI,	11	53, 63, 62, 63, 44,	52.7	6.7
50 mM TBAI		54, 51, 49, 47, 46, 48		
100mM LiTFSI,	4	29, 32, 30, 32	30.8	1.7
33 mM TBAI				
1.2 mM LiTFSI	6	80, 85, 73, 85, 83, 85	81.8	4.3
2.5 mM LiTFSI	5	75, 57, 56, 72, 68	65.6	7.8
3.8 mM LiTFSI	3	62, 64, 67	64.3	2.1

Data used for Fig.2A and Fig.2B.



**Fig. S7:** Evolution of *G*' (full square) and *G*'' (empty circle) as a function of time *t* as the temperature *T* (dots) decreases. Experiments used to study the influence of  $[TFSI^-]/[I^-]$  ratio on  $T_g$  ([1(Br)<sub>2</sub>] = 1.3 mM in pentanol for al samples). A) [LITFSI] = [TBAI] = 100 mM (measured  $T_g = 77^{\circ}$ C), B) [LITFSI]= 100 mM and [TBAI] = 50 mM (measured  $T_g = 51^{\circ}$ C), C) [LITFSI]= 100 mM and [TBAI] = 33 mM (measured  $T_g = 30^{\circ}$ C).



**Fig. S8** Evolution of *G'* (full square) and *G''* (empty circle) as a function of time *t* as the temperature *T* (dots) decreases. Experiments used to study the influence of  $[TFSI^-]/[Br^-]$  ratio on  $T_g$  ([1(Br)<sub>2</sub>] = 1.3 mM in pentanol for al samples). A) [LITFSI] = 0.6 mM (measured  $T_g \simeq 90^{\circ}$ C), B) [LITFSI] = 1.3 mM (measured  $T_g = 85^{\circ}$ C), C) [LITFSI] = 2.5 mM (measured  $T_g = 72^{\circ}$ C), d) [LITFSI] = 3.8 mM (measured  $T_g = 62^{\circ}$ C).



**Fig. S9** Evolution of *G*' (full square) and *G*'' (empty circle) as a function of time t as the temperature *T* (dot) decreases. A) Experiment used to study the influence of  $[TFSI^-]/[I^-]$  ratio on  $T_g$ , G'>G'' at  $T \sim 20$  °C ( $[1(Br)_2] = 1.3 \text{ mM}$ , [LITFSI] = 100 mM, [TBAI] = 25 mM in pentanol) B) Experiment used to study the influence of  $[TFSI^-]/[Br^-]$  ratio on  $T_g$ , G'>G'' at  $T \sim 55$  °C ( $[1(Br)_2] = 1.3 \text{ mM}$ , [LITFSI] = 1.3 mM, [LITFSI] = 6.3 mM in pentanol)

#### Electrochemical Impedance Spectroscopy

The electronic impedance spectroscopy measurements have been performed in a homemade two electrodes conductivity cell of 5 mm length (noted I) using, the two electrodes were 1 cm diameter Pt disk (of area *S*). The theoretical value of the cell constant is then:

$$\left[\frac{l}{s}\right]_{theo} = \frac{5.10^{-3}}{3.14(5.10^{-3})^2} = \frac{1}{3.14 \times 5.10^{-3}} = 63.7 \ m^{-1}$$

The cell constant was calculated after performing PEIS measurements reference KCl solutions from Radiometer analytical of respective conductivities (0.1408 S.m<sup>-1</sup>, 1.285 S.m<sup>-1</sup> and 11.13 S.m<sup>-1</sup>). The obtained cell constant  $\kappa$  = 62.8  $\pm$  0.7 m<sup>-1</sup> was used to calculate the ionic conductivities of the samples through the relation  $\sigma = \kappa/R$ .



Fig. S10 Determination of the conductivity cell constant. Black squares: resistance measured for reference KCl solutions (Radiometer analytical) of known conductivity. Red line: result of the linear regression, the slope of the line corresponds to the cell constant  $\kappa = I/S$ .

For all samples the obtained Nyquist plots were fitted using the Randles-like equivalent circuit described in Fig. 8B in the frequency range 100 mHz to 100 kHz. The ionic conductivity values plotted in Fig. 3 were calculated using R1 value using the relation  $\sigma = \kappa/R1$ . The R1 values are reported in Table S2.

 Table S2 Ionic resistance of gels and salt solutions formed in pentanol for various ionic compositions.

State	Composition	R1 (Ω)
Gel	0.2wt% <b>1</b> (Br) <sub>2</sub> , 10 mM LiTFSI, 5 mM TBAI	8900
Sol	10 mM LiTFSI, 5 mM TBAI	8800
Gel	0.2wt% <b>1</b> (Br) <sub>2</sub> , 25 mM LiTFSI, 12.5 mM TBAI	3700
Sol	25 mM LiTFSI, 12.5 mM TBAI	3800
Gel	0.2wt% <b>1</b> (Br) <sub>2</sub> , 50 mM LiTFSI, 25 mM TBAI	2600
Sol	50 mM LiTFSI, 25 mM TBAI	2600
Gel	0.2wt% <b>1</b> (Br) <sub>2</sub> , 100 mM LiTFSI, 50 mM TBAI	1200
Sol	100 mM LiTFSI, 50 mM TBAI	1200
Gel	0.2wt% <b>1</b> (Br) <sub>2</sub> , 200 mM LiTFSI, 100 mM TBAI	690
Suspension	200 mM LiTFSI, 100 mM TBAI	Not studied due to crystallization
		of the electrolyte upon cooling

For each sample the values of R1, Q2, R2 and W2 were found to remain constant over an hour timescale after gelation. As the resistance R1 merely corresponds to the concentration in salts, the obtained values were reproducible. The uncertainty on R1 can be considered around 5% of the indicated value, merely due to variations in the positioning of the electrodes. The values of R2 and W2 were however way more fluctuating over the different experiments performed. For the most studied gel composition (0.2 wt%  $1(Br)_2$ , 100 mM LiTFSI, 50 mM TBAI), R2 could vary between 5k $\Omega$  and 10 k $\Omega$ , W2 could vary from 2000 to 10000 (1-j)/(2 $\pi$ f)<sup>0.5</sup>. Such a great variability is most likely to come from a difference in the self-assembly of the gelator at the electrode/gel interface between the different samples. For this reason, the voltammogram represented on Fig. S11 was performed on the exact same gel sample as the one used for Fig 8.

Cyclic voltammetry experiments have been performed in the conductivity cell by applying a potential sweep between the two Pt electrodes ( $\emptyset$  = 1cm) at a slow scan rate (5 mV/s). This experiment shows that the potential applied during the PEIS experiments (highlighted in orange on Fig S.11) corresponds to the foot of the viologen-based 1<sup>st</sup> reduction wave. In this range the *i*=f(*E*) curve could be fitted with a 1/R2 line, confirming that R2 is the charge transfer resistance corresponding to the reduction of the viologen according to the Butler Volmer theory.



**Fig. S11** Cyclic voltammetry experiment (5mV/s on Pt) performed in the conductivity cell on a gel sample ([ $1(Br)_2$ ] = 1.3 mM, [LiTFSI] = 100 mM, [TBAI] = 50mM in pentanol). Voltage is indicated using the second electrode of the cell as reference. Potential sweep starts at  $E_{OC}$  which is the same potential at which the PEIS measurements were carried on. The PEIS potential range is highlighted in orange. The blue line indicates the slope corresponding to a charge transfer resistance of 6000  $\Omega$ .

# Anion metathesis protocol and gelation conditions:

 $\mathbf{1}$ (TFSI)<sub>2</sub> was synthesize to investigate the properties of gels containing only TFSI and no other anions. All the other gels discussed in the article were obtained upon addition of LiTFI and/or TBAI to a suspension of  $\mathbf{1}$ (Br)<sub>2</sub> in a given solvent.

All gels containing mixtures of salts have been obtained upon heating suspensions of  $1(Br)_2$ , LiTFSi and/or TBAI or TBABr in a given solvent up to reaching full solubilization of all the solids introduced.

Pure  $1(TFSI)_2$  was obtained from  $1(Br)_2$  as a product of an anion metathesis procedure described below :

55 mg (0.04 3mmol) of  $1(Br)_2$  was stirred under reflux in 50mL MeOH. After one hour the solid was fully dissolved and 118mg of LiTFSI (0.41 mmol, 9.5 molar eq) were added. The mix was stirred at room temperature for two hours and was then concentrated under reduced pressure to afford a white precipitate. 50 mL of water were added to the mix, then the solid was filtered and thoroughly washed with water. The solid was dried under vacuum to afford 50 mg of  $1(TFSI)_2$  as a white solid.

Solvant	Wt%	T <sub>sol</sub>	Resistance to inversion	Homogeneity	Transparence	Resistance to inversion after mixing
1-Butanol	2.4%	100°C	Yes	No	No	No
1-Pentanol	1.3%	90°C	Yes	No	No	No
1-Hexanol	1.8%	100°C	Yes	No	No	No
1-Heptanol	2.5%	100°C	Yes	No	No	No
1-Octanol	2.4%	110°C	Yes	No	No	No

Table S3 Summary of screening gelation conditions with 1(TFSI)<sub>2</sub>

## Absorbance spectroscopy and circular dichroism





**Fig. S12:** Influence of the concentration in  $1(Br)_2$  on the absorbance spectra collected for gel samples. Pentanol, [LiTFSI] = 100 mM, [TBAI] = 50 mM. 1 mm quartz cuvette (left). Picture of the corresponding samples (right).



**Fig. S13**: A) UV-vis absorbance spectra recorded over time during the cooling/gelation of a hot solution of  $1(Br)_2$  and LiTFSI down to 20 °C ( $[1(Br)_2] = 1.3 \text{ mM}$ , [LiTFSI] = 2.5 mM in pentanol). B) Influence of the concentration in  $1(Br)_2$  on the absorbance spectrum of gels containing LiTFSI and TBABr as additives (for all samples [LiTFSI] = 100 mM, [TBABr] = 50 mM in pentanol). Yellow curve:  $[1(Br)_2] = 2.5 \text{ mM}$  (gel). Green curve:  $[1(Br)_2] = 1.3 \text{ mM}$  (gel). Light blue curve:  $[1(Br)_2] = 0.6 \text{ mM}$  (gel). Dark blue curve:  $[1(Br)_2] = 0.3 \text{ mM}$  (suspension that could not pass the inversion test). C)  $g_{abs}$  spectra collected for gels obtained from  $1(Br)_2$  and LiTFSI in pentanol ( $[1(Br)_2] = 1.3 \text{ mM}$ , [LiTFSI] = 2.5 mM) D) Influence of LiTFSI on the spectroscopic properties of gels obtained from  $1(Br)_2$  ( $[1(Br)_2] = 1.3 \text{ mM}$  in pentanol for all samples). Dark blue curve: [LiTFSI] = 0.6 mM. Light blue curve: [LiTFSI] = 1.3 mM. Green curve: [LiTFSI] = 2.5 mM in pentanol for all samples). Dark blue curve: [LiTFSI] = 0.6 mM. Light blue curve: [LiTFSI] = 1.3 mM. Green curve: [LiTFSI] = 2.5 mM. Yellow curve: [LiTFSI] = 5.0 mM. The sample corresponding to the yellow curve does not form a gel after an heating cooling cycle. Experiments for graph A, B, C and D were performed in 1mm quartz cuvette.



**Figure S.14**: Left: Influence of  $[TFSI^-]/[I^-]$  ratio on the UV-Vis absorbance spectra of gels and suspensions. Dark blue curve: [TBAI] = 100 mM (gel). Light blue curve: [TBAI] = 50 mM (gel). Green curve: [TBAI] = 33 mM (gel). Yellow curve: [TBAI] = 25 mM (suspension). Right: Visual aspect of  $\mathbf{1}(Br)_2$  gel ( $[TFSI^-] = [I^-] = 100 \text{ mM}$ ) and  $\mathbf{1}(Br)_2$  suspension ( $[TFSI^-] = 4 [I^-] = 100 \text{ mM}$ ). For all samples [LiTFSI] = 100 mM and  $[\mathbf{1}(Br)_2] = 1.3 \text{ mM}$  in pentanol, experiments were performed in 1 mm quartz cuvette



**Fig. S15** A) Evolution of the ECD spectra of  $0.1 \text{mM} \mathbf{1}(\text{Br})_2$  solution in pentanol for increasing concentrations in TFSI<sup>-</sup>. Dark blue: no LiTFSI; light blue: [TFSI<sup>-</sup>] = 0.2 mM; yellow: [TFSI<sup>-</sup>] = 0.5 mM; green: [TFSI<sup>-</sup>] = 1.0 mM. B) Evolution of the UV-Vis absorbance spectra of  $0.1 \text{mM} \mathbf{1}(\text{Br})_2$  solution in pentanol for increasing concentrations in TFSI<sup>-</sup>. Dark blue: no LiTFSI; light blue: [TFSI<sup>-</sup>] = 0.2 mM; yellow: [TFSI<sup>-</sup>] = 0.2 mM; yellow: [TFSI<sup>-</sup>] = 0.5 mM; green: [TFSI<sup>-</sup>] = 1.0 mM. Experiments were performed in 1 mm quartz cuvette