

**Electronic Supplementary Information**  
**Insights about the Ability of Folate based Supramolecular Gels to Act as**  
**Targeted Therapeutic Agents**

*Carla Rizzo<sup>a,‡</sup> Patrizia Cancemi,<sup>b,‡</sup> Miriam Buttacavoli,<sup>b</sup> Gianluca Di Cara,<sup>b</sup> Cesare  
D'Amico,<sup>b</sup> Floriana Billeci,<sup>a,c</sup> Salvatore Marullo,<sup>a</sup>  
Francesca D'Anna<sup>a\*</sup>*

<sup>a</sup>*Università degli Studi di Palermo, Dipartimento STEBICEF, Sezione di Chimica, Viale delle  
Scienze Ed. 17, 90128 Palermo (Italy)*

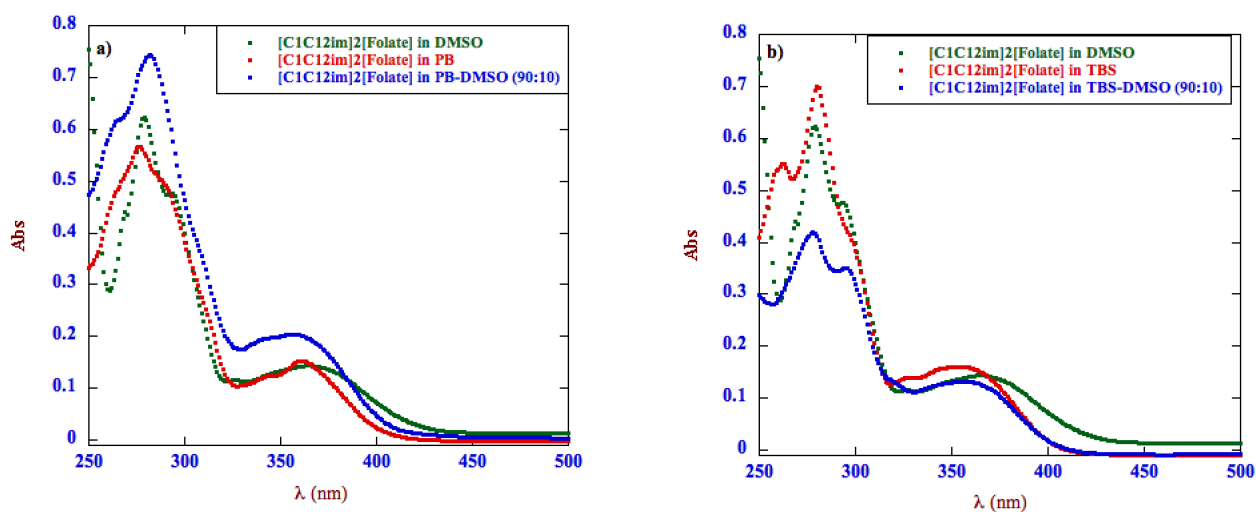
<sup>b</sup>*Università degli Studi di Palermo, Dipartimento STEBICEF, Sezione di Biologia Cellulare, Viale  
delle Scienze Ed. 16, 90128 Palermo (Italy)*

<sup>c</sup>*Until March 2022*

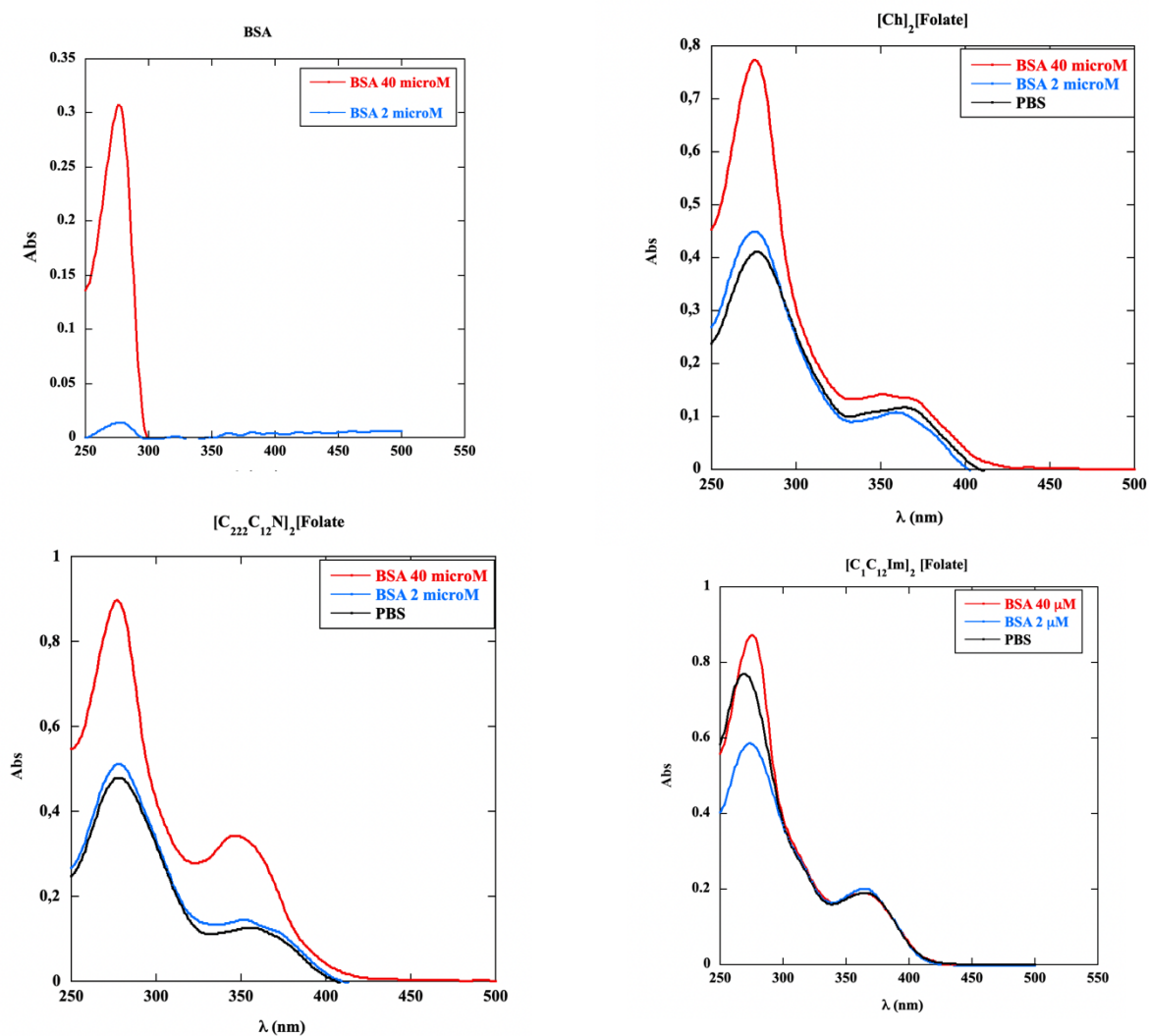
<sup>‡</sup>These authors contributed equally

\*Corresponding author: Prof. F. D'Anna. E-mail: [francesca.danna@unipa.it](mailto:francesca.danna@unipa.it)

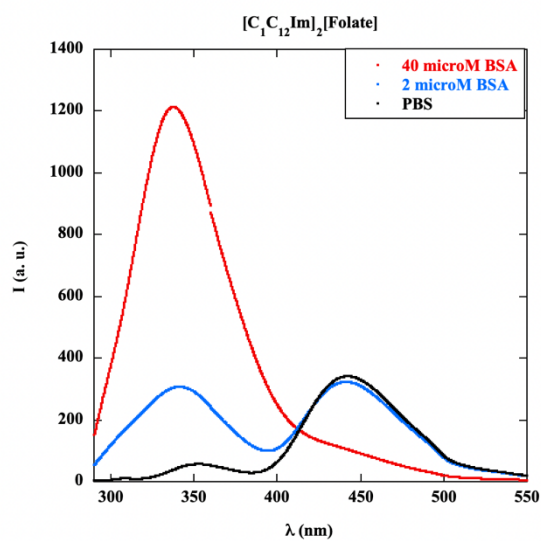
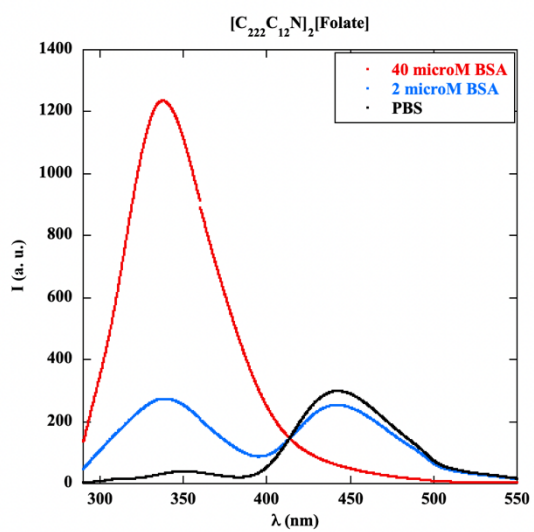
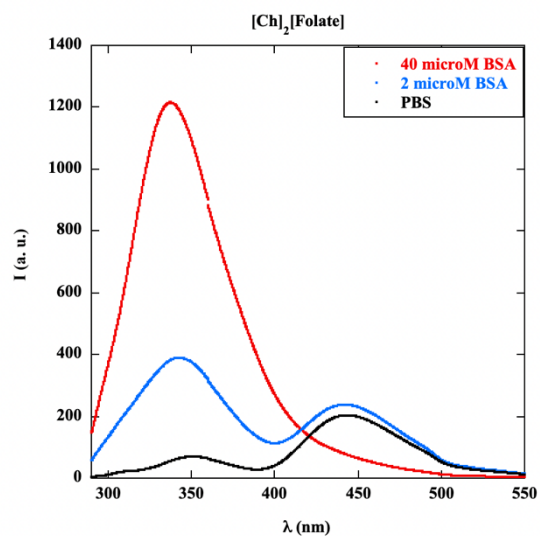
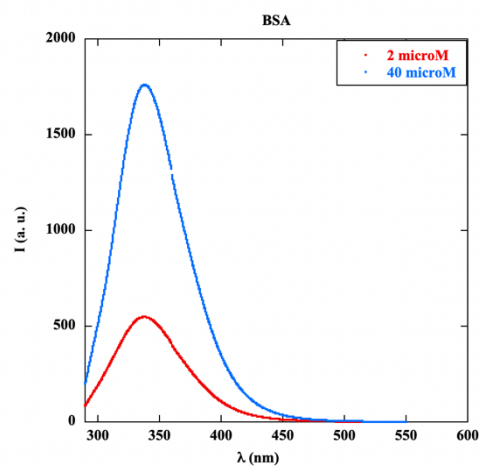
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**Figure S1.** UV spectra of  $[C_1C_{12}Im]_2[Folate]$  in solution at  $10^{-4} M$ .

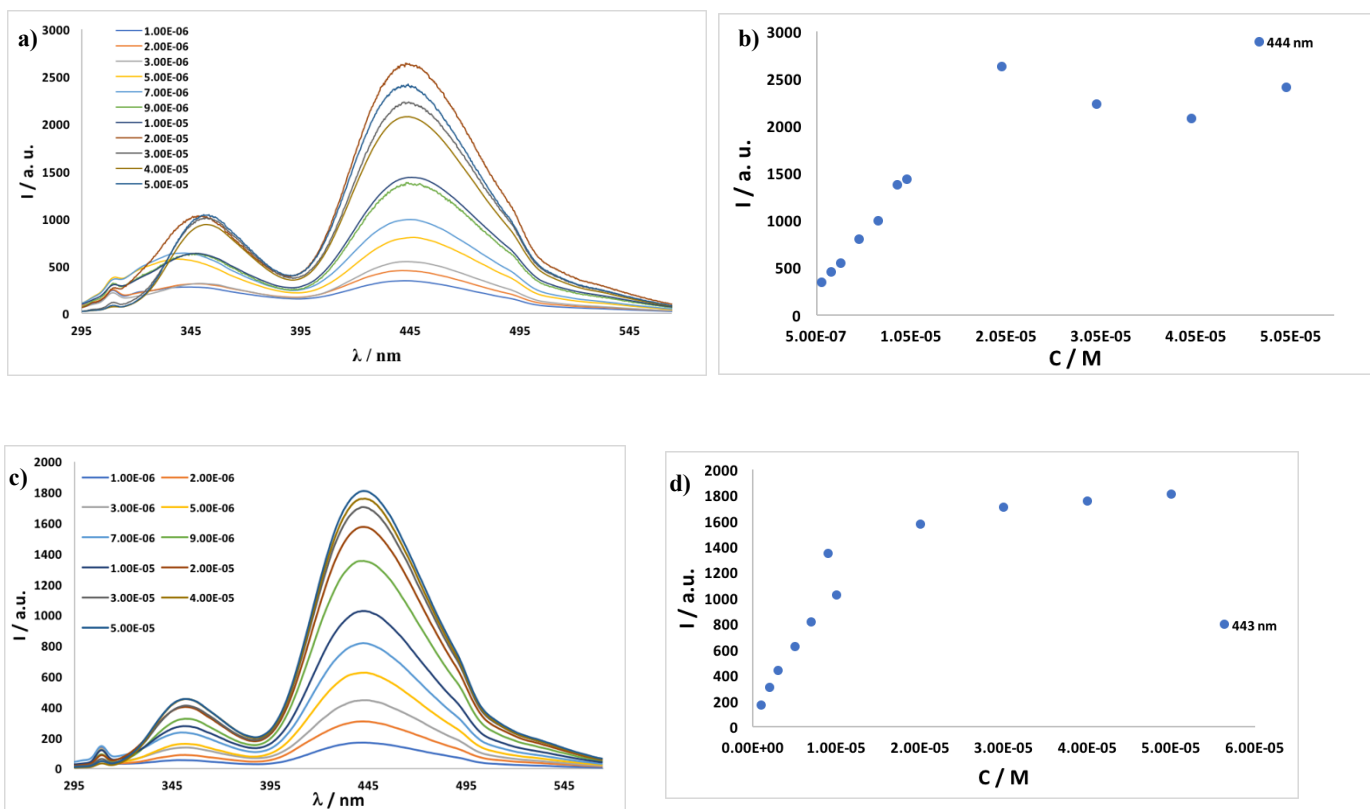


**Figure S2.** UV spectra of organic salts (0.0001 M), in PBS solution, in the presence of increasing amount of BSA (2 and 40  $\mu M$ ).

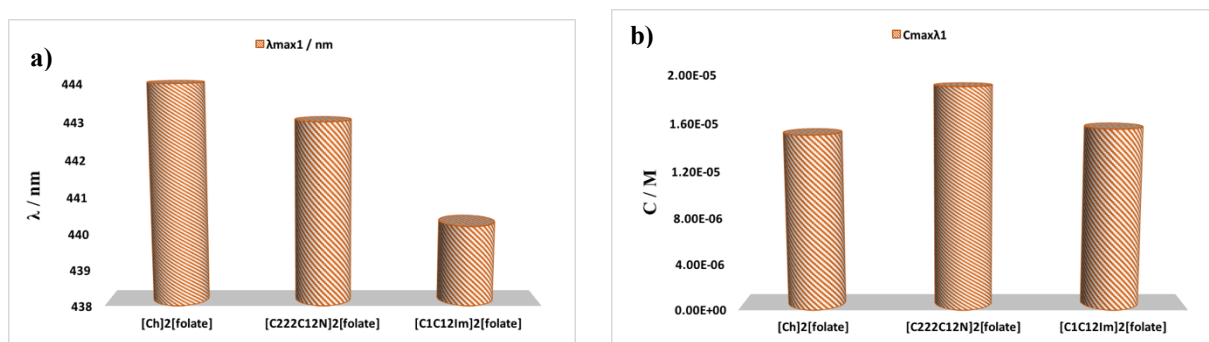


**Figure S3.** Fluorescence spectra of organic salts (0.0001 M), in PBS solution, in the presence of increasing amount of BSA (2 and 40  $\mu\text{M}$ ).

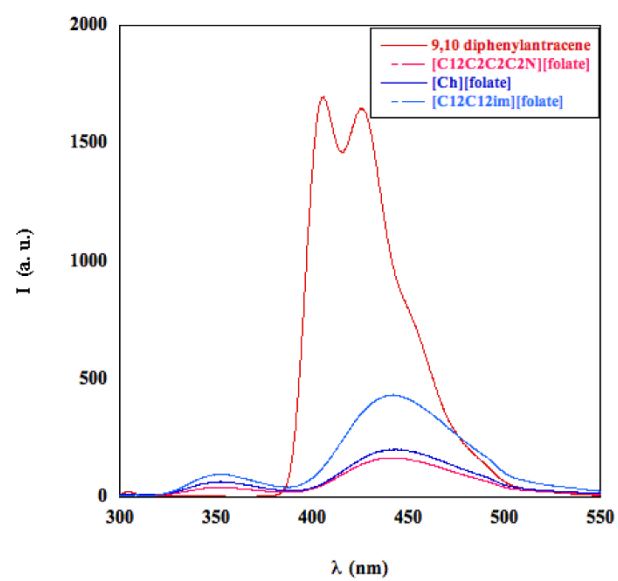




**Figure S4.** Fluorescence spectra of **a)**  $[\text{Ch}]_2[\text{Folate}]$  and **c)**  $[\text{C}_{222}\text{C}_{12}\text{N}]_2[\text{Folate}]$  in PBS at variable concentrations; fluorescence intensity as function of solution concentration for **c)**  $[\text{Ch}]_2[\text{Folate}]$  and **d)**  $[\text{C}_{222}\text{C}_{12}\text{N}]_2[\text{Folate}]$ .



**Figure S5.** **a)** Wavelength of fluorescence maxima of organic salts in PBS; **b)** critical aggregation concentration obtained from fluorescence intensity as function of salt concentration.



**Figure S6.** Emission spectra of [Folate]-based salt and 9,10-diphenylanthracene, in ethanol solution, at  $2 \cdot 10^{-5}$  M.

**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in PB**

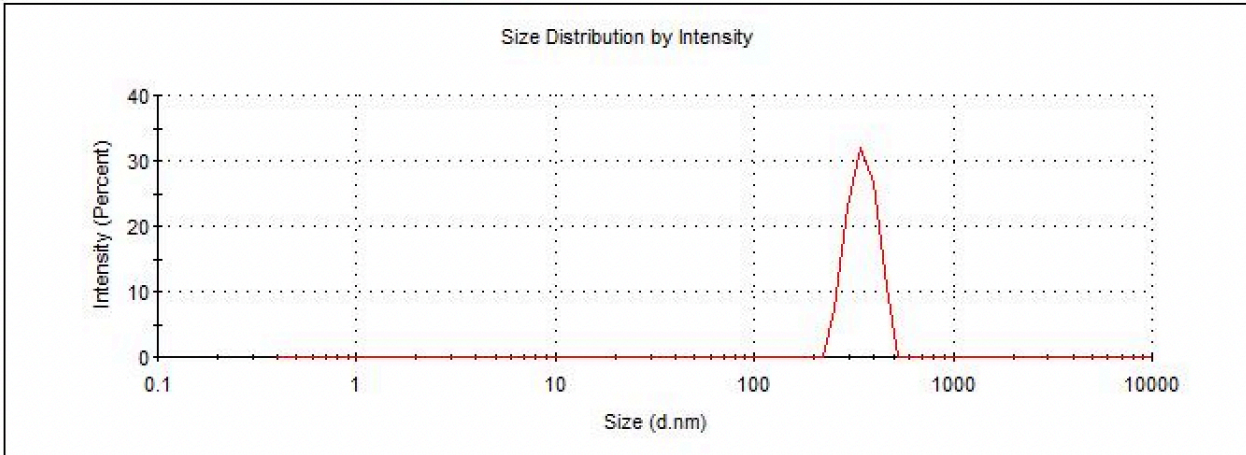
**Z-Average (d.nm): 650,7**

**Pdl: 0,545**

**Intercept: 0,876**

	Size (d.nm):	% Intensity:	St Dev (d.nm):
<b>Peak 1:</b>	352,0	100,0	56,90
<b>Peak 2:</b>	0,000	0,0	0,000
<b>Peak 3:</b>	0,000	0,0	0,000

**Result quality : Refer to quality report**



**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in PB/DMSO**

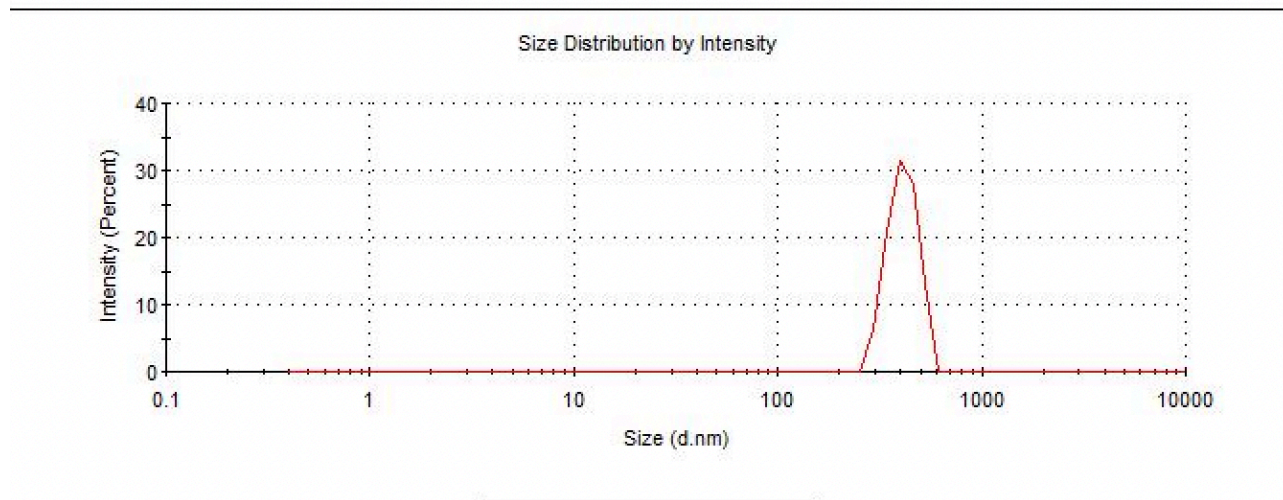
**Z-Average (d.nm): 748,5**

**Pdl: 0,575**

**Intercept: 0,862**

	Size (d.nm):	% Intensity:	St Dev (d.nm):
<b>Peak 1:</b>	413,7	100,0	66,82
<b>Peak 2:</b>	0,000	0,0	0,000
<b>Peak 3:</b>	0,000	0,0	0,000

**Result quality : Refer to quality report**



**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in PBS**

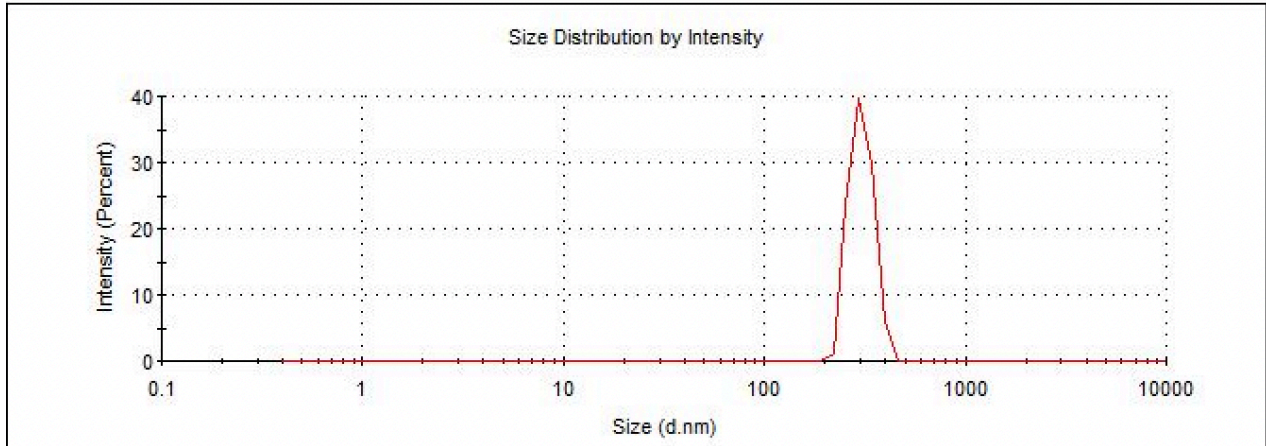
**Z-Average (d.nm): 741,0**

**Pdl: 0,618**

**Intercept: 0,881**

**Result quality : Refer to quality report**

	Size (d.nm):	% Intensity:	St Dev (d.nm):
<b>Peak 1:</b>	304,8	100,0	40,13
<b>Peak 2:</b>	0,000	0,0	0,000
<b>Peak 3:</b>	0,000	0,0	0,000



**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in PBS/DMSO**

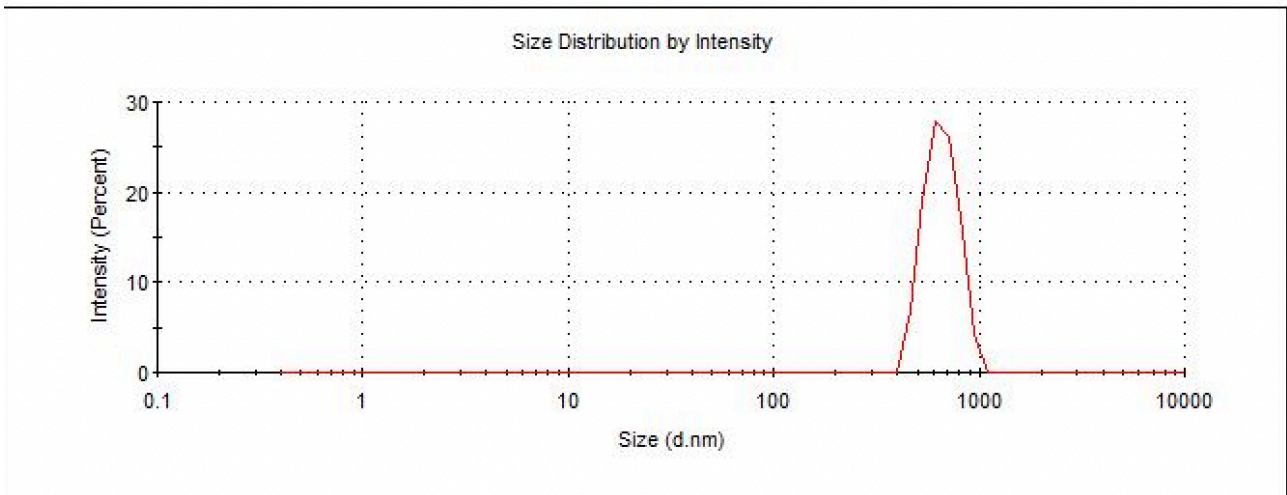
**Z-Average (d.nm): 979,3**

**Pdl: 0,494**

**Intercept: 0,666**

**Result quality : Refer to quality report**

	Size (d.nm):	% Intensity:	St Dev (d.nm):
<b>Peak 1:</b>	661,5	100,0	123,6
<b>Peak 2:</b>	0,000	0,0	0,000
<b>Peak 3:</b>	0,000	0,0	0,000

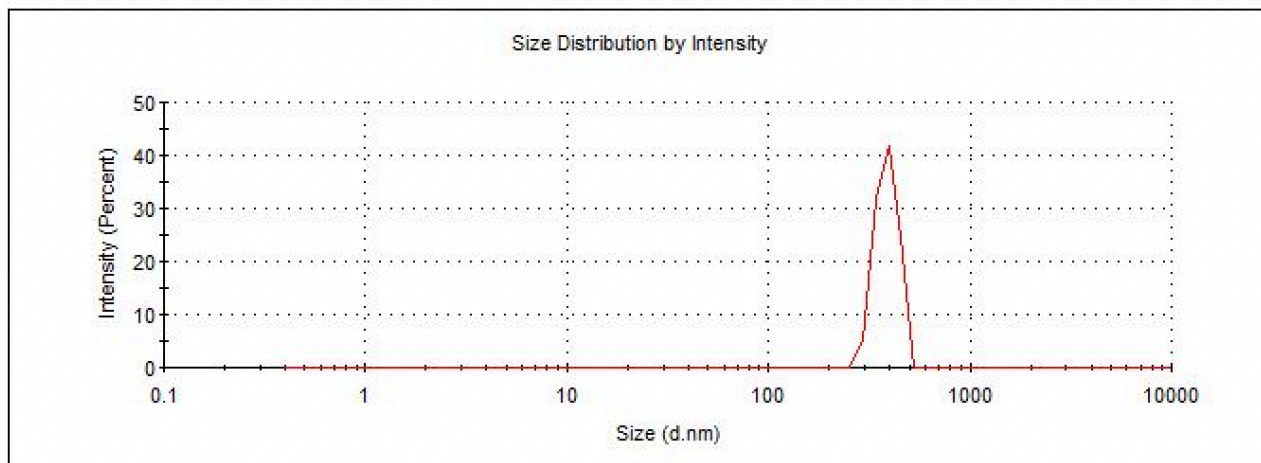




**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in Tris**

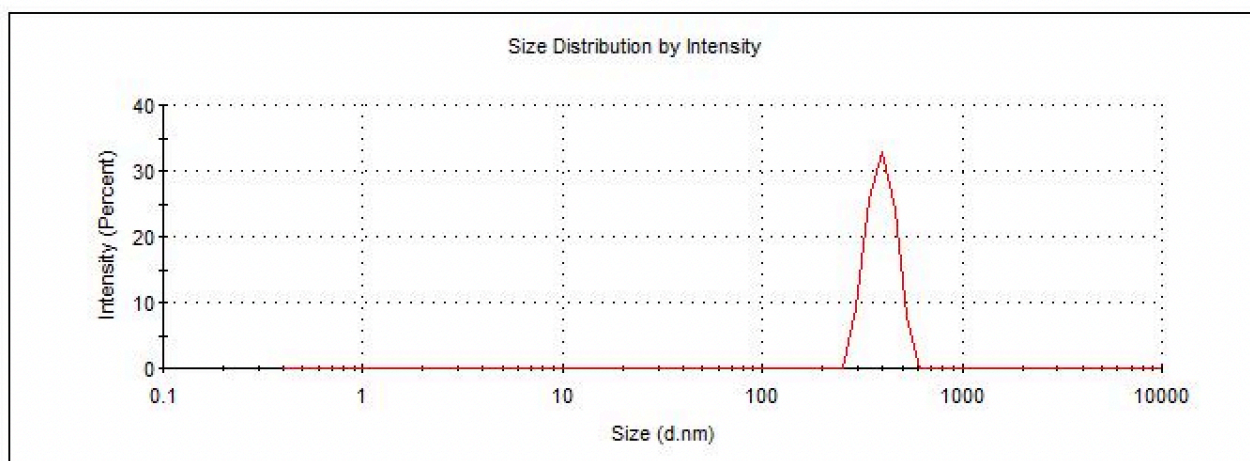
	Size (d.nm):	% Intensity:	St Dev (d.nm):
<b>Z-Average (d.nm):</b> 929,1	<b>Peak 1:</b> 387,3	100,0	46,90
<b>Pdl:</b> 0,668	<b>Peak 2:</b> 0,000	0,0	0,000
<b>Intercept:</b> 0,885	<b>Peak 3:</b> 0,000	0,0	0,000

**Result quality :** Refer to quality report

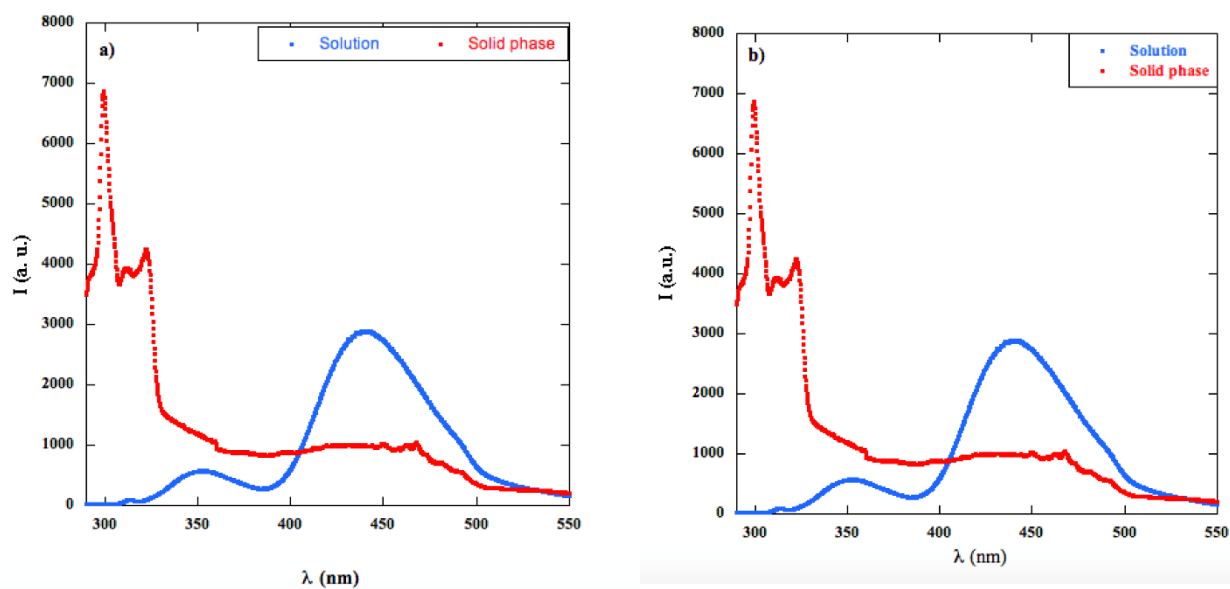
**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in Tris/DMSO**

	Size (d.nm):	% Intensity:	St Dev (d.nm):
<b>Z-Average (d.nm):</b> 646,3	<b>Peak 1:</b> 398,7	100,0	64,00
<b>Pdl:</b> 0,507	<b>Peak 2:</b> 0,000	0,0	0,000
<b>Intercept:</b> 0,716	<b>Peak 3:</b> 0,000	0,0	0,000

**Result quality :** Refer to quality report



**Figure S7.** Apparent hydrodynamic diameter distribution functions obtained in buffer and buffer/DMSO for [C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] from DLS experiments.



**Figure S8.** Superimposed fluorescence spectra, in PBS solution ( $3 \cdot 10^{-5}$  M) and solid phase, for **a)**  $[\text{Ch}]_2[\text{Folate}]$  and **b)**  $[\text{C}_{22}\text{C}_{12}\text{N}]_2[\text{Folate}]$ .

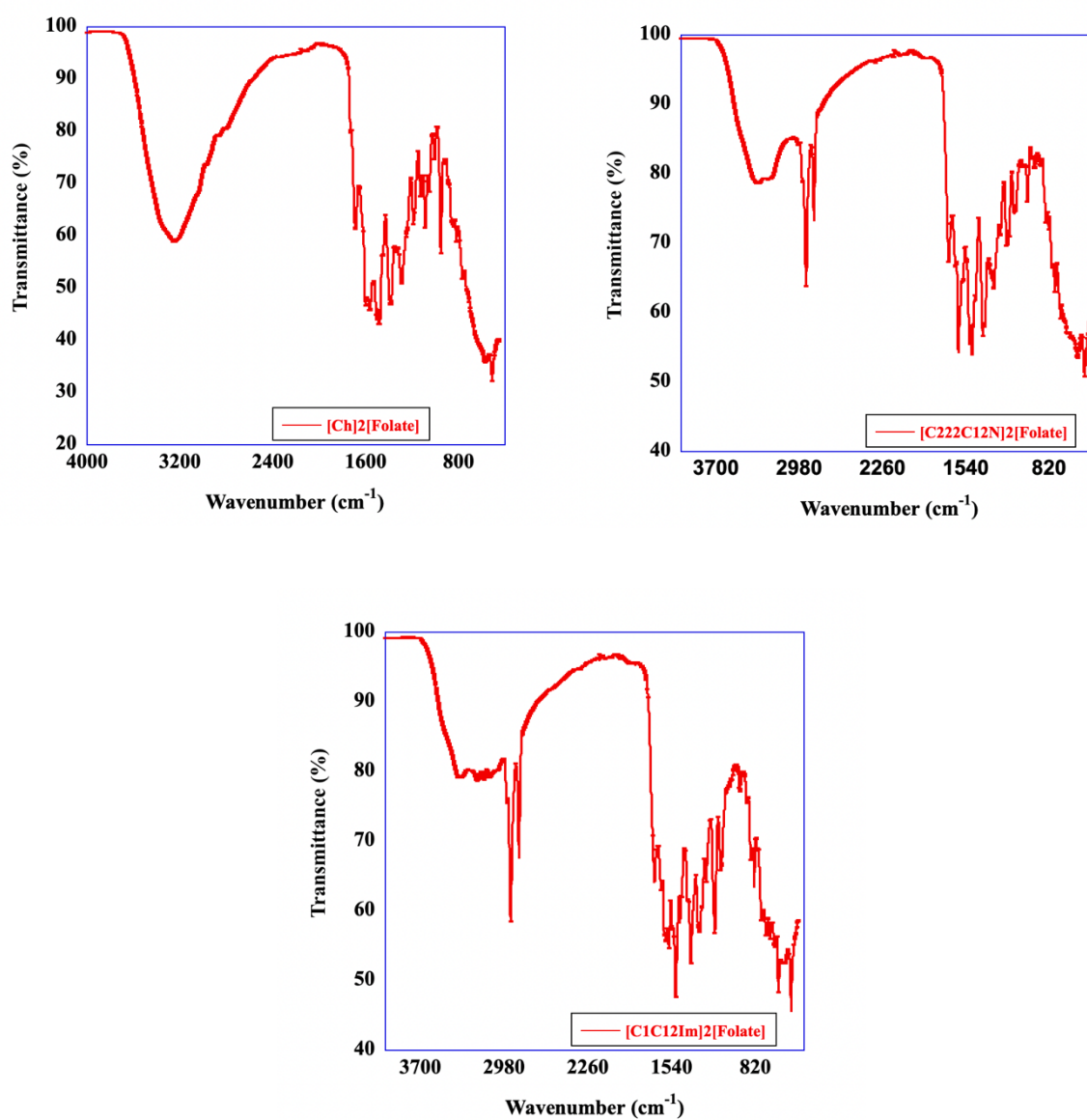
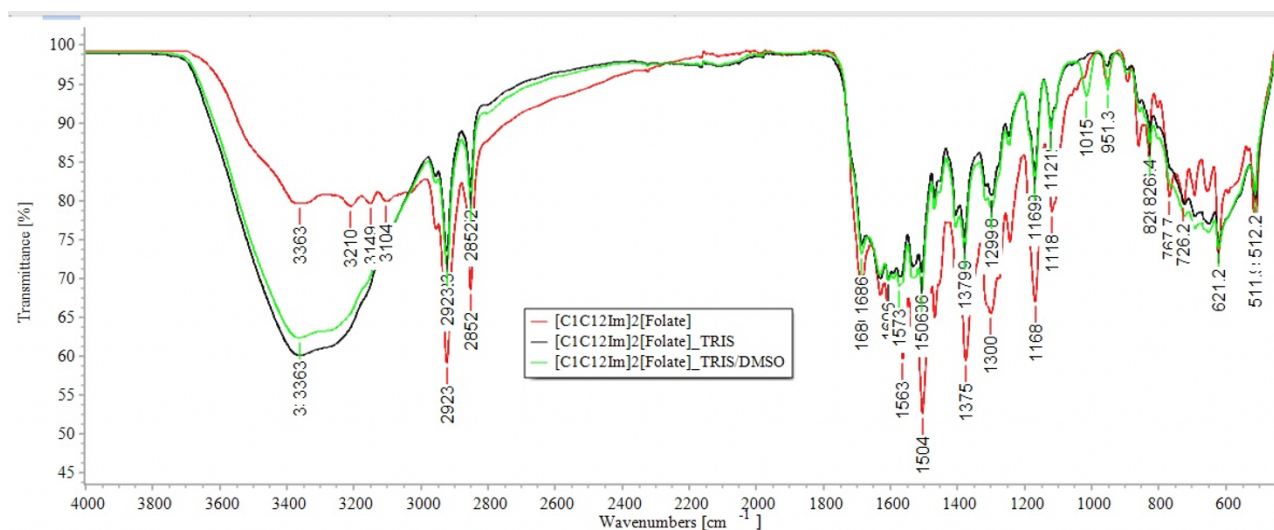
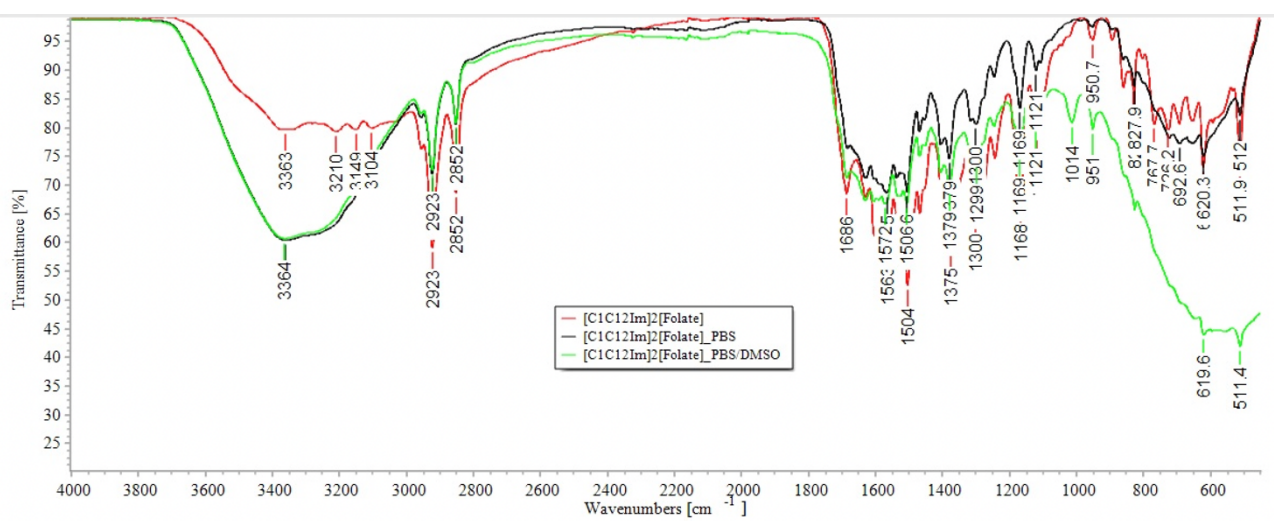
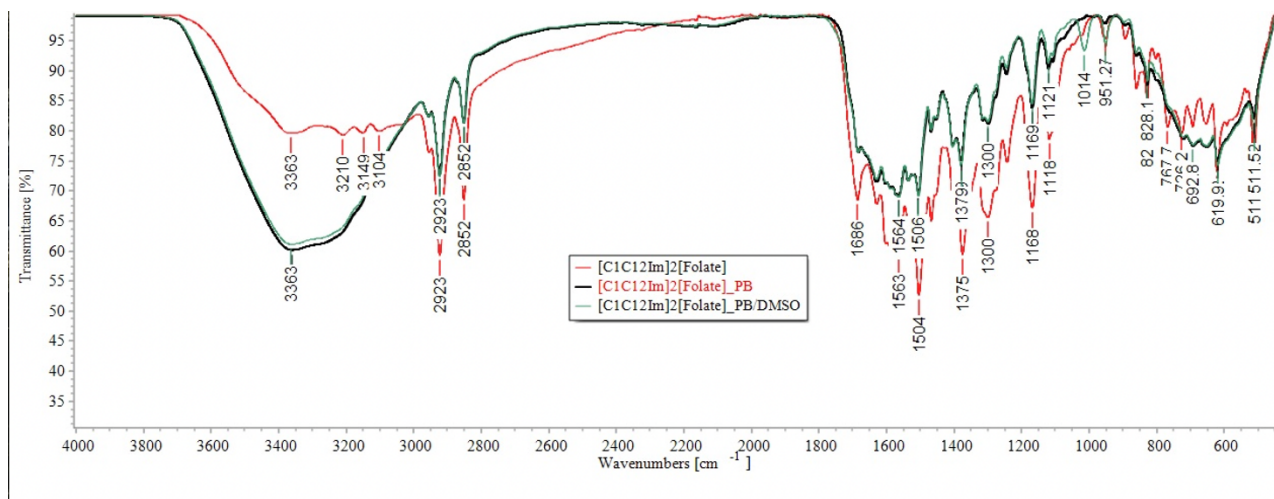


Figure S9. ATR-FTIR spectra of organic salts.



**Figure S10.** Superimposed ATR-FTIR spectra of [C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] and corresponding gel phases. IR spectra were plotted with Spectragryph.



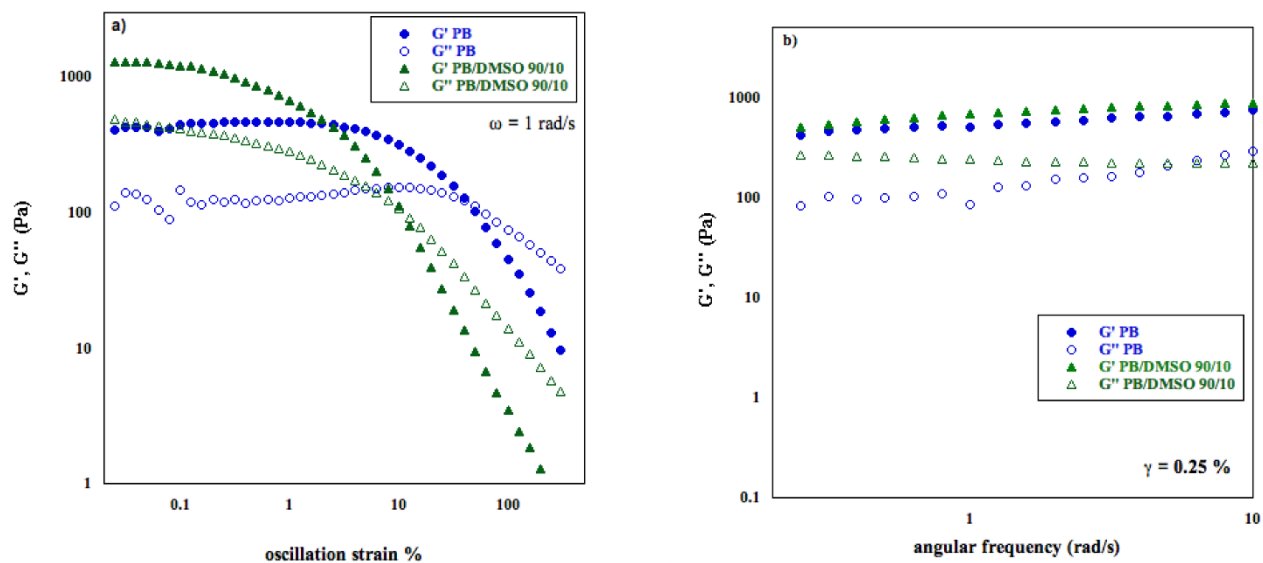


Figure S11. Strain and frequency sweeps of hydrogels formed by  $[\text{C}_{11}\text{C}_{12}\text{Im}]_2[\text{folate}]$ , in PB and PB/DMSO at 6 wt % .

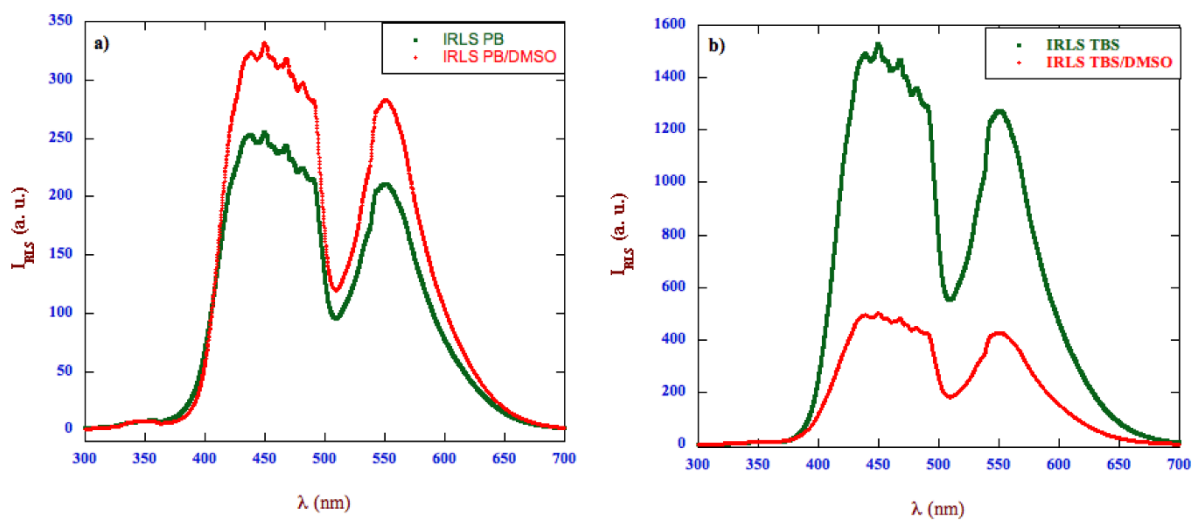
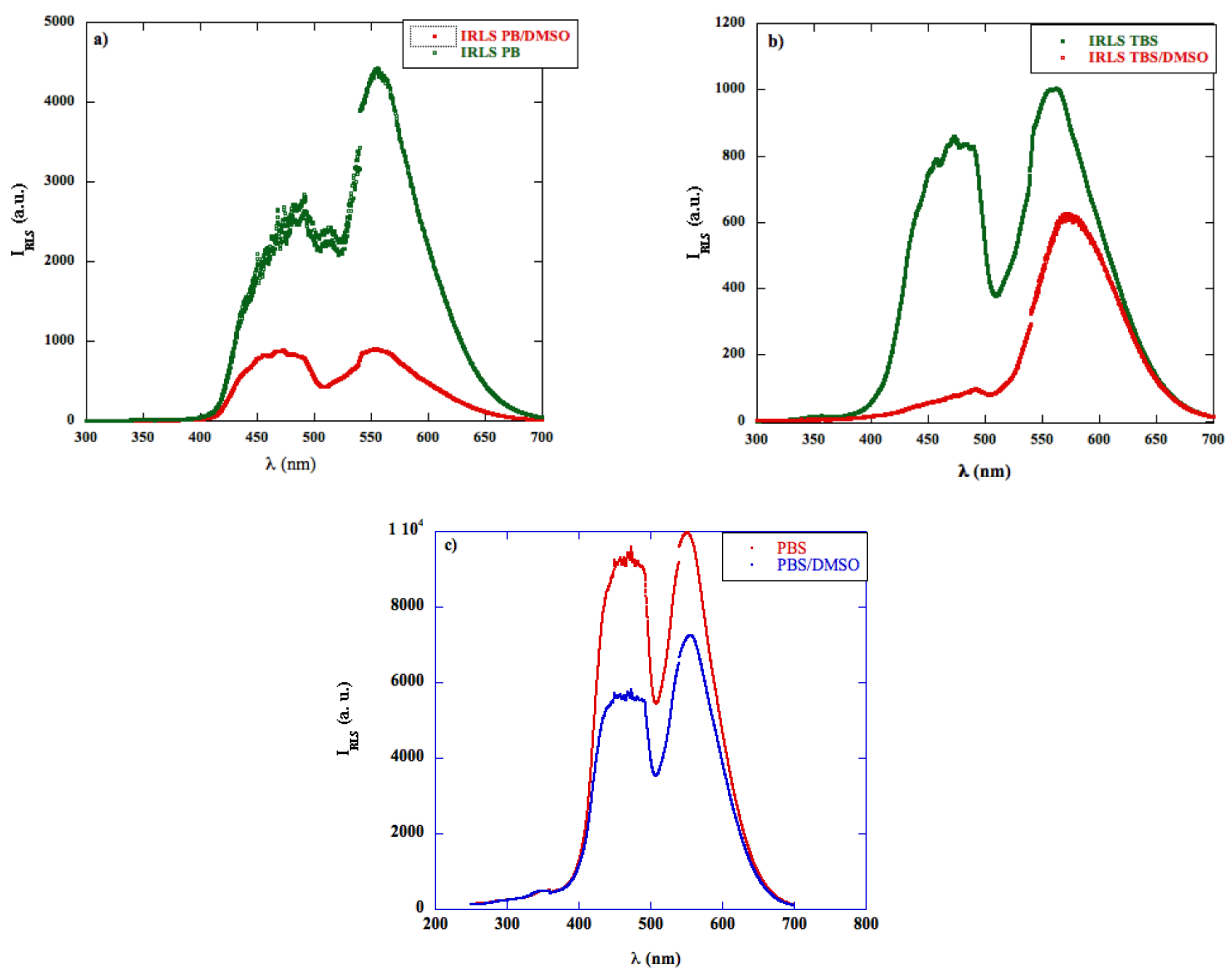
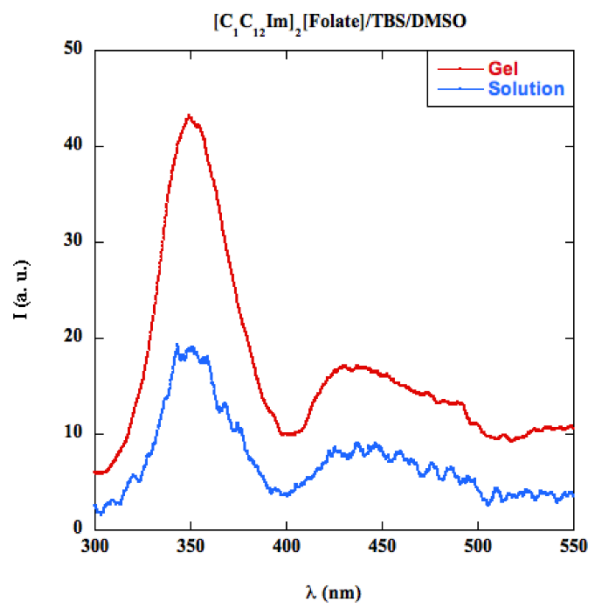
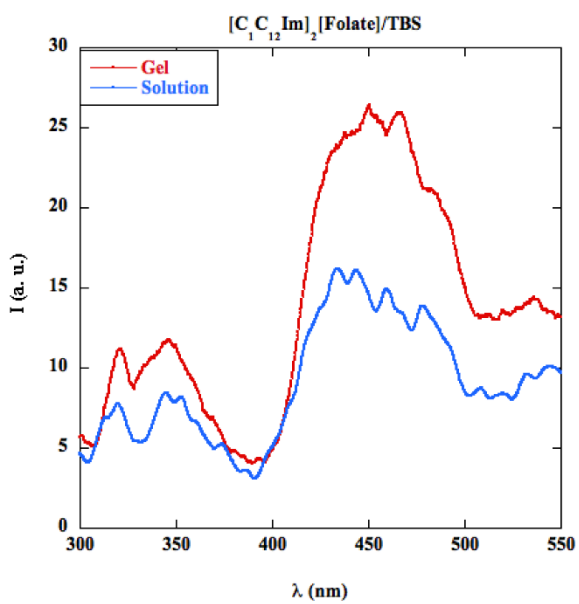
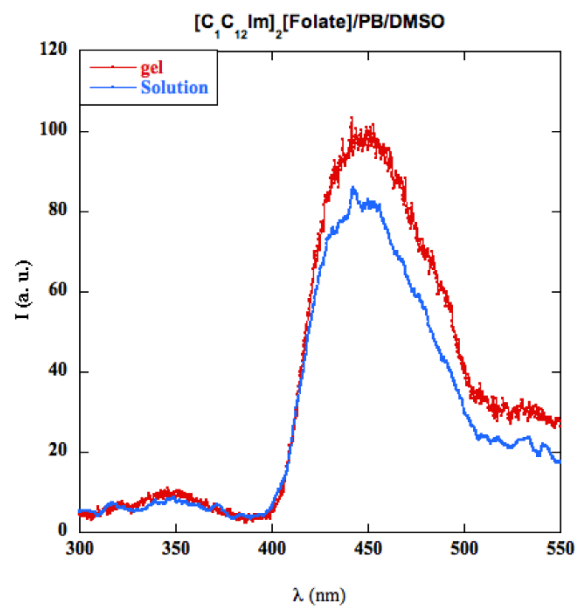
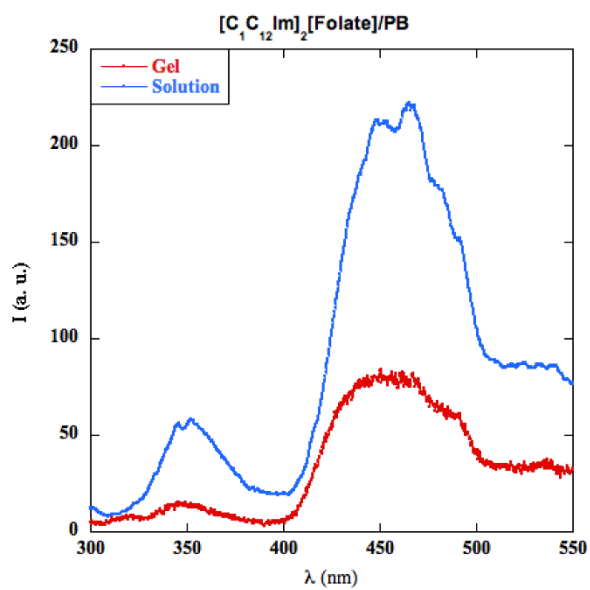
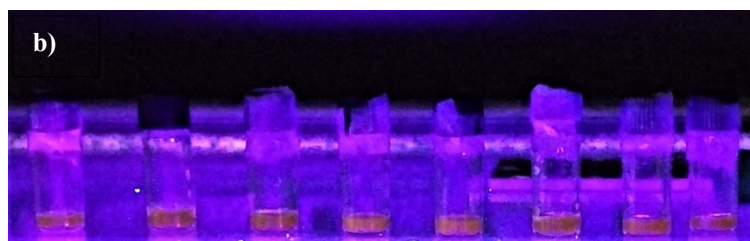
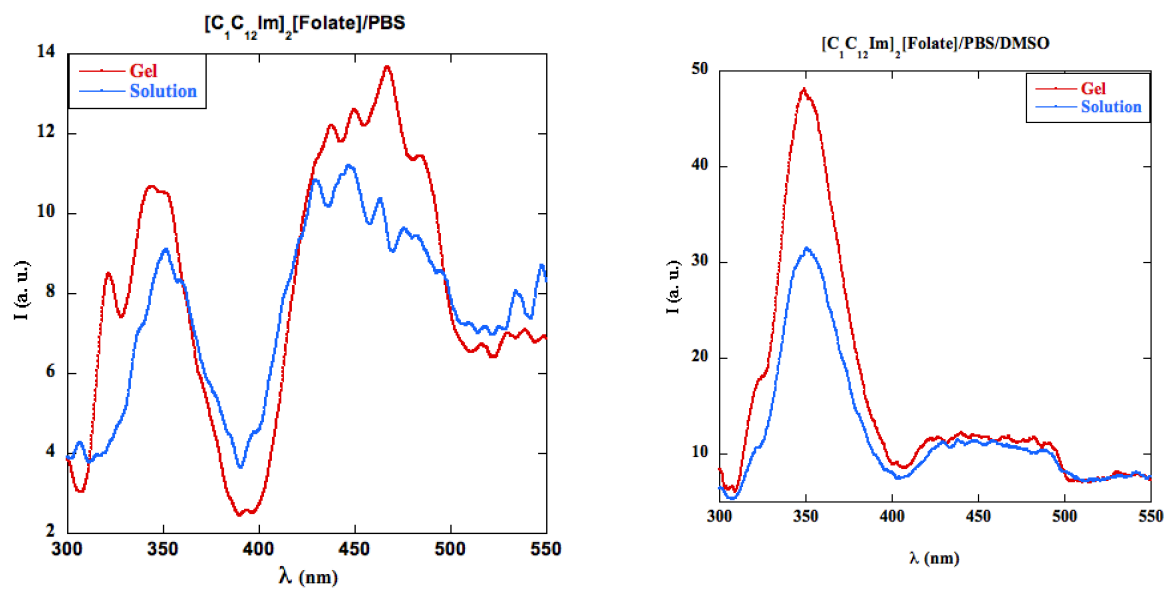


Figure S12. RLS Spectra of  $[\text{C}_{11}\text{C}_{12}\text{Im}]_2[\text{Folate}]$  solution ( $2.6 \cdot 10^{-4} \text{ M}$ ) in a) PB and PB/DMSO and b) TBS and TBS/DMSO.  $I_{\text{RLS}}$  at 450 nm, for different solutions at 450 nm, are displayed in Table 5.

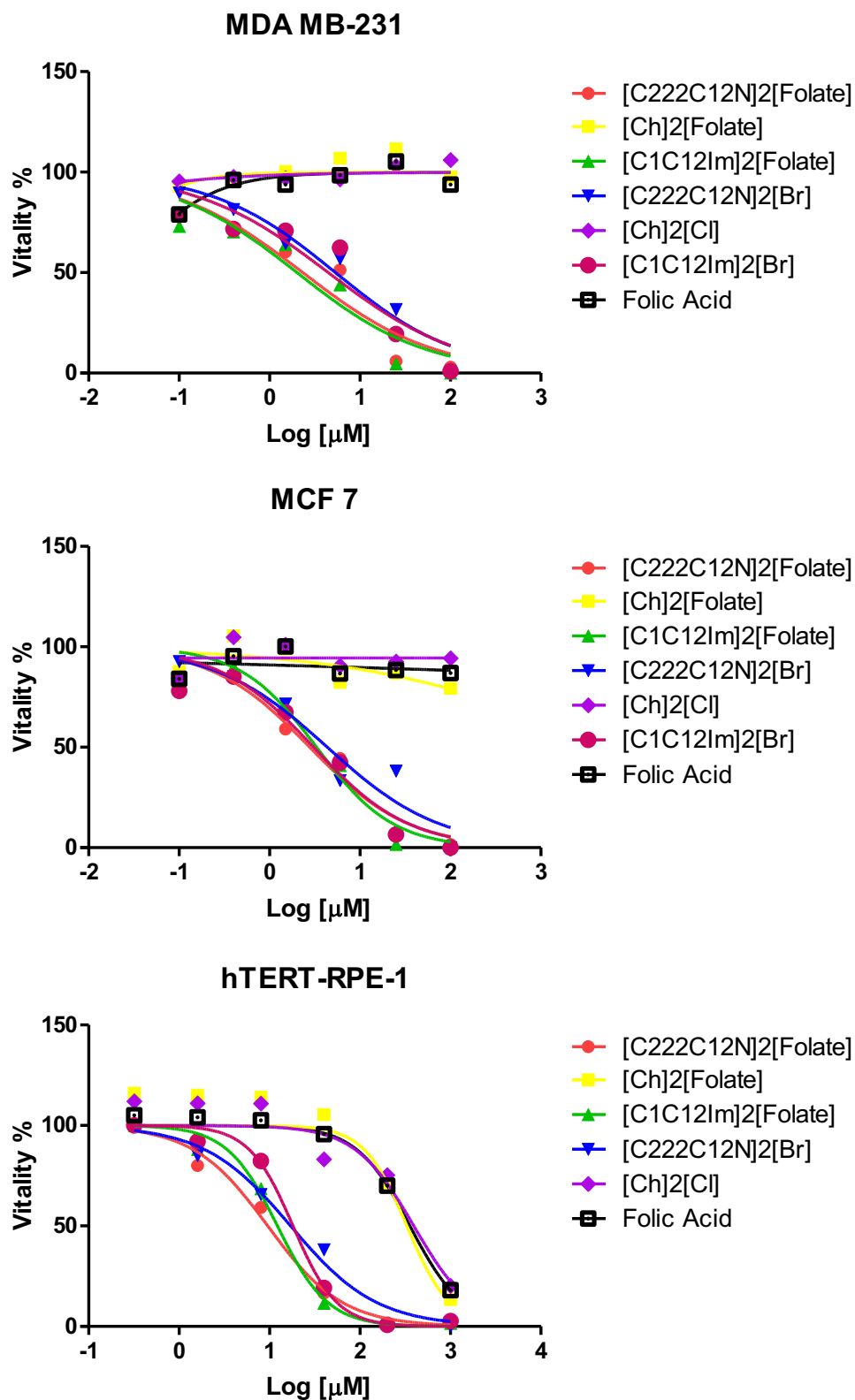


**Figure S13.** RLS Spectra of  $[C_{1}C_{12}Im]_{2}[Folate]$  gel at 6 wt % in **a)** PB and PB/DMSO and **b)** TBS and TBS/DMSO. IRLS at 470 nm are displayed in Table S5.





**Figure S14.** Fluorescence emission spectra of the hot solution and corresponding gel of  $[C_{12}Im]_2[Folate]$  at 6 wt %; **b)** Picture of  $[C_{12}Im]_2[Folate]$  gels irradiated at 365 nm.

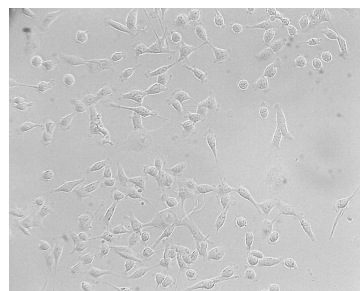
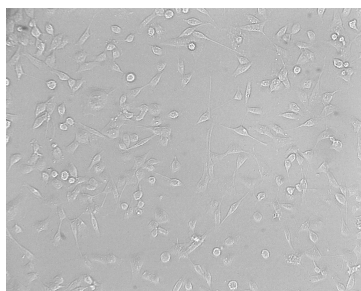


**Figure S15.** Sigmoidal cytotoxicity curves of treated MDA MB-231, MCF 7 and hTERT-RPE-1 cells for 24 h, obtained by plotting the cell percentage inhibition versus the logarithmic of salts concentration.

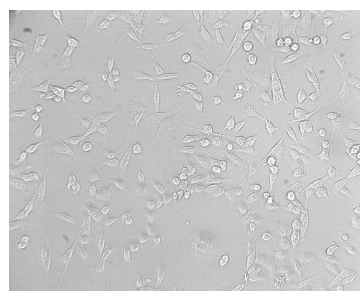
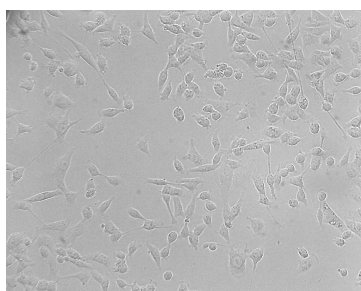
**A**

MDA-MB-231

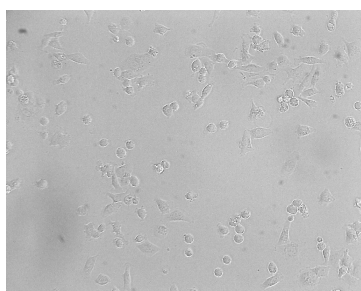
**Control**



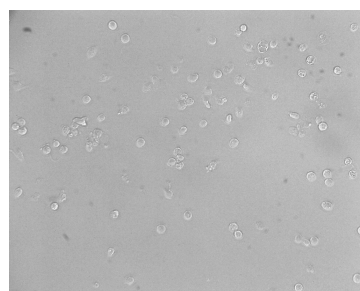
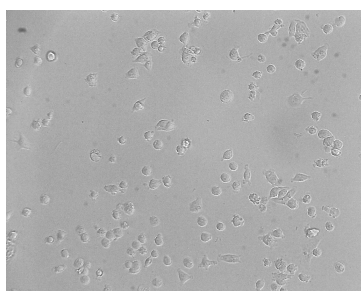
**Folic Acid**



**[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub>[Folate]**

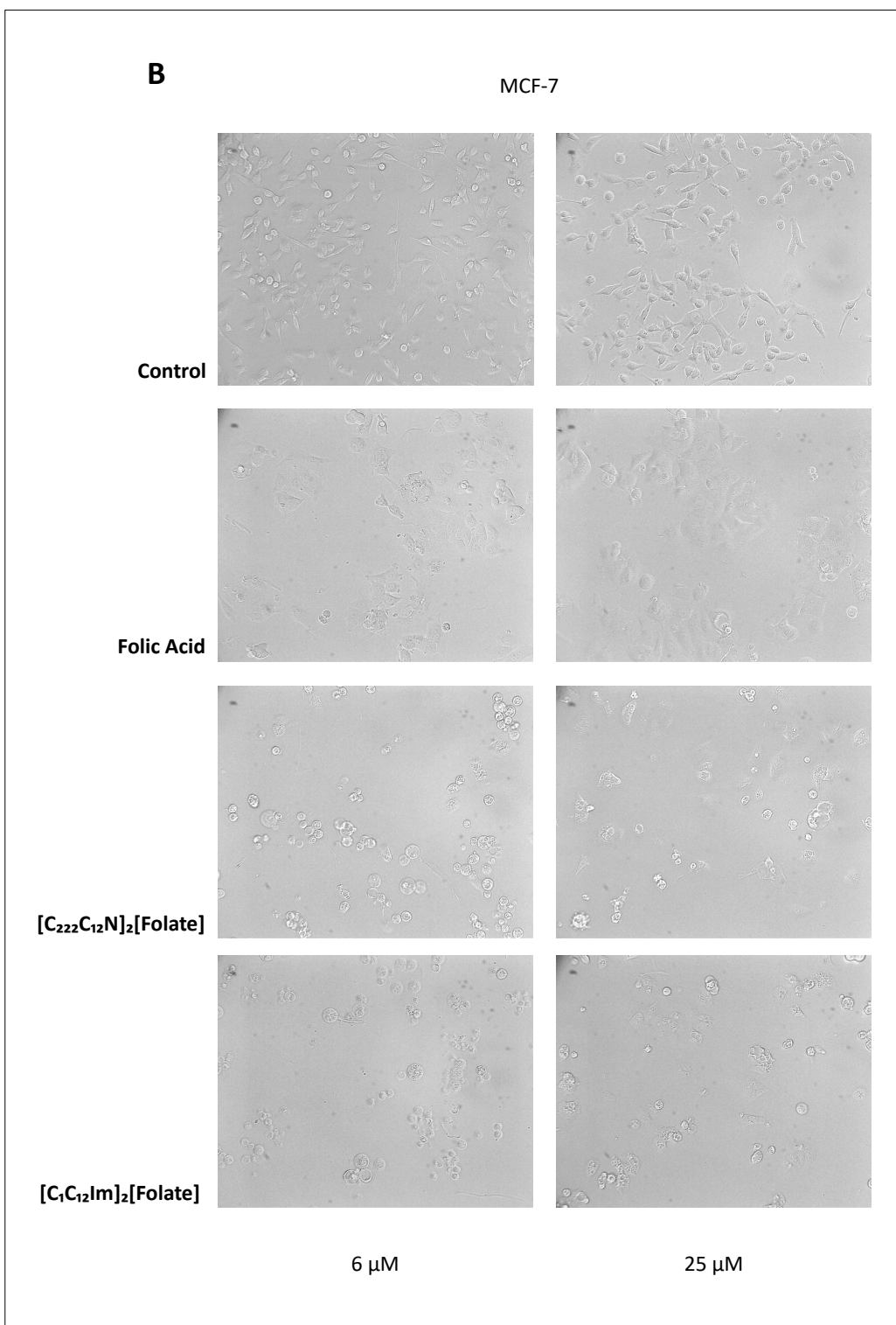


**[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate]**

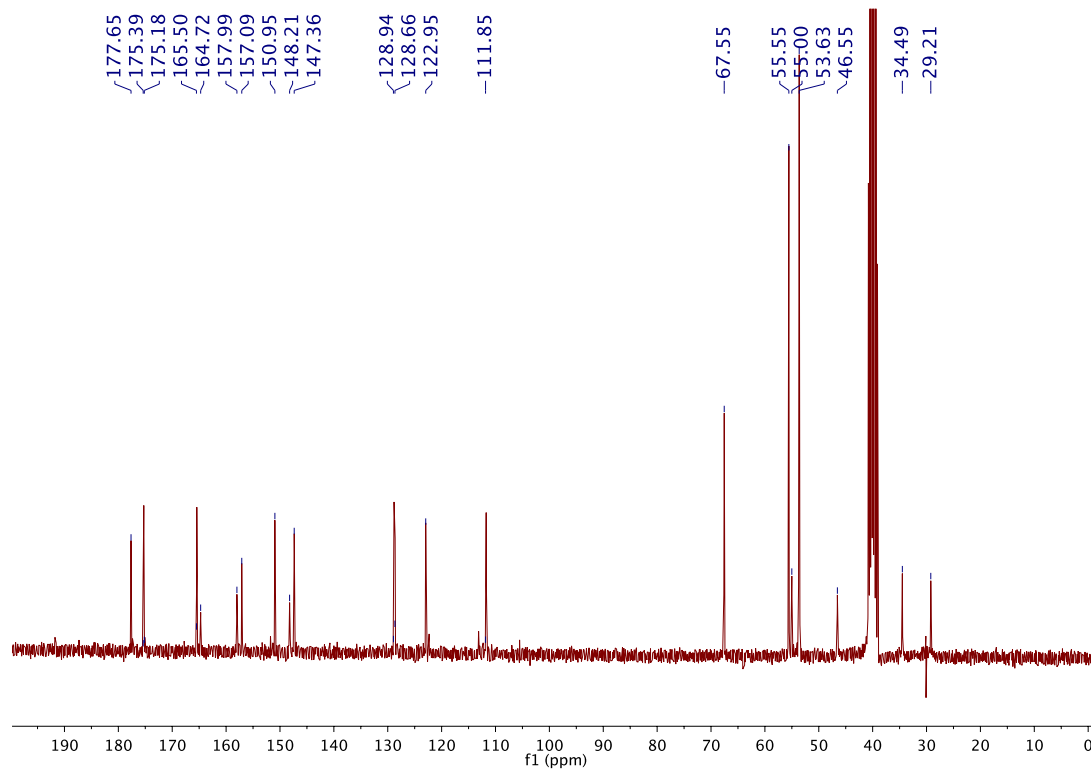
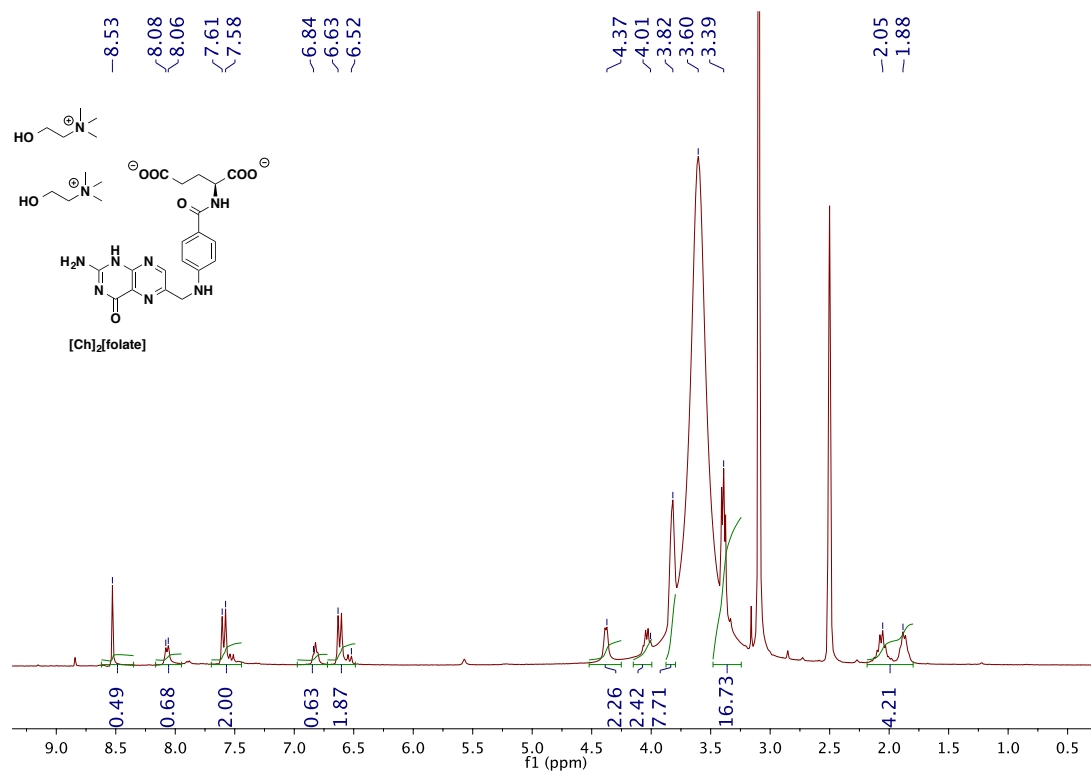


6 μM

25 μM

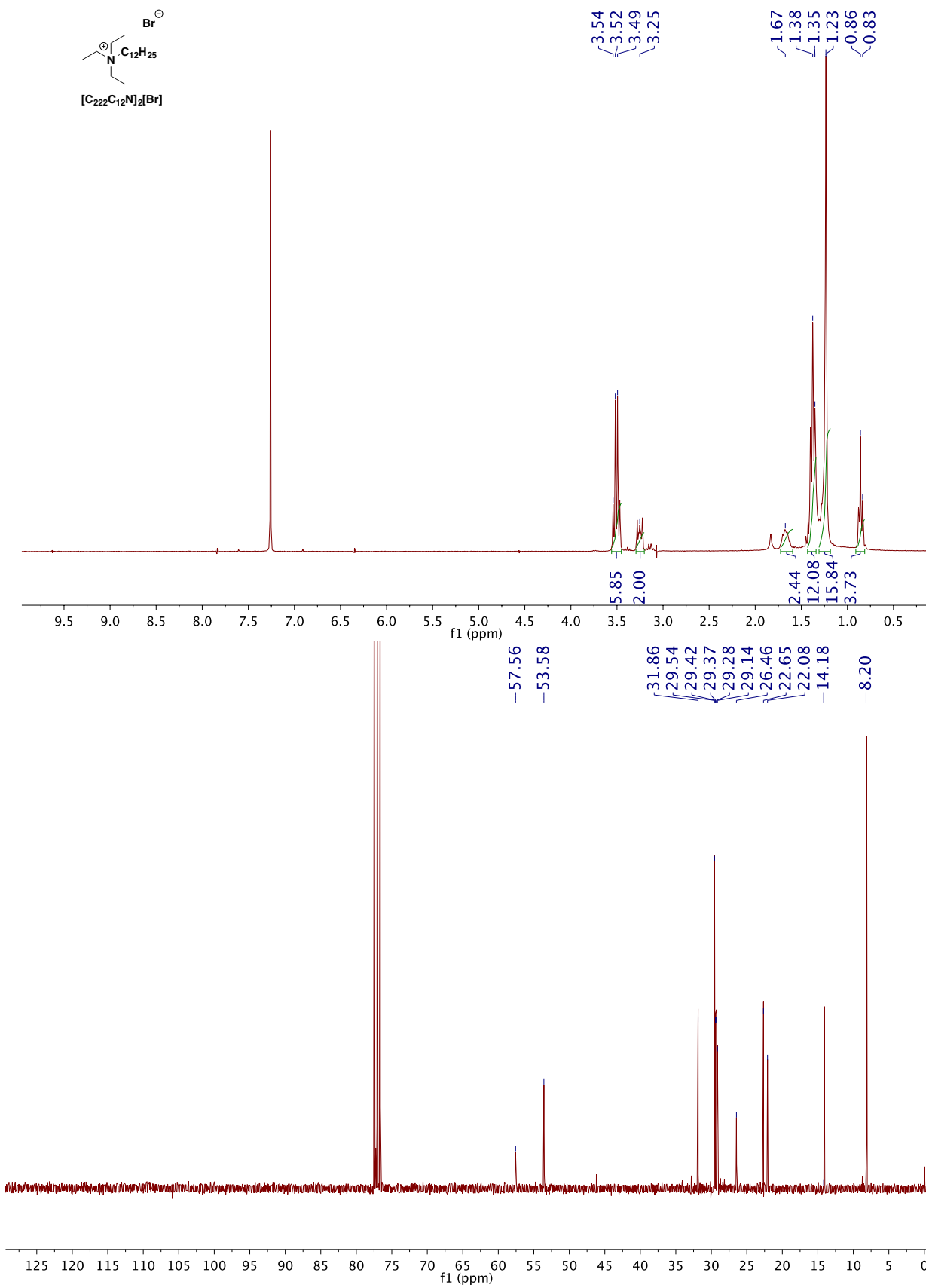
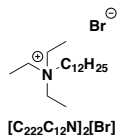


**Figure S16.** Inverted-phase contrast micrographs of MDA-MB-231 (A) and MCF-7 (B) cells treated for 24h with 6 and 25 μM of Folic Acid, [C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub>[Folate] and [C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate]. Magnification 100X.

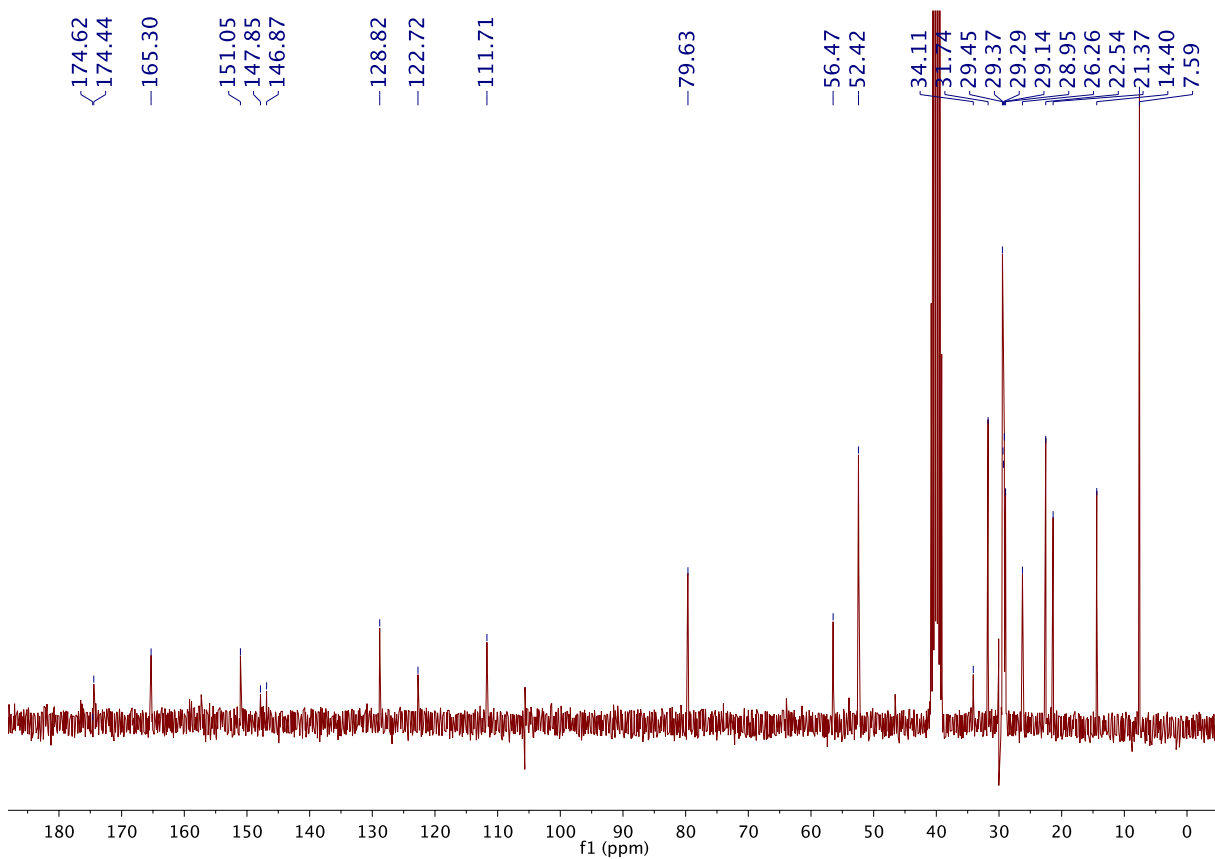
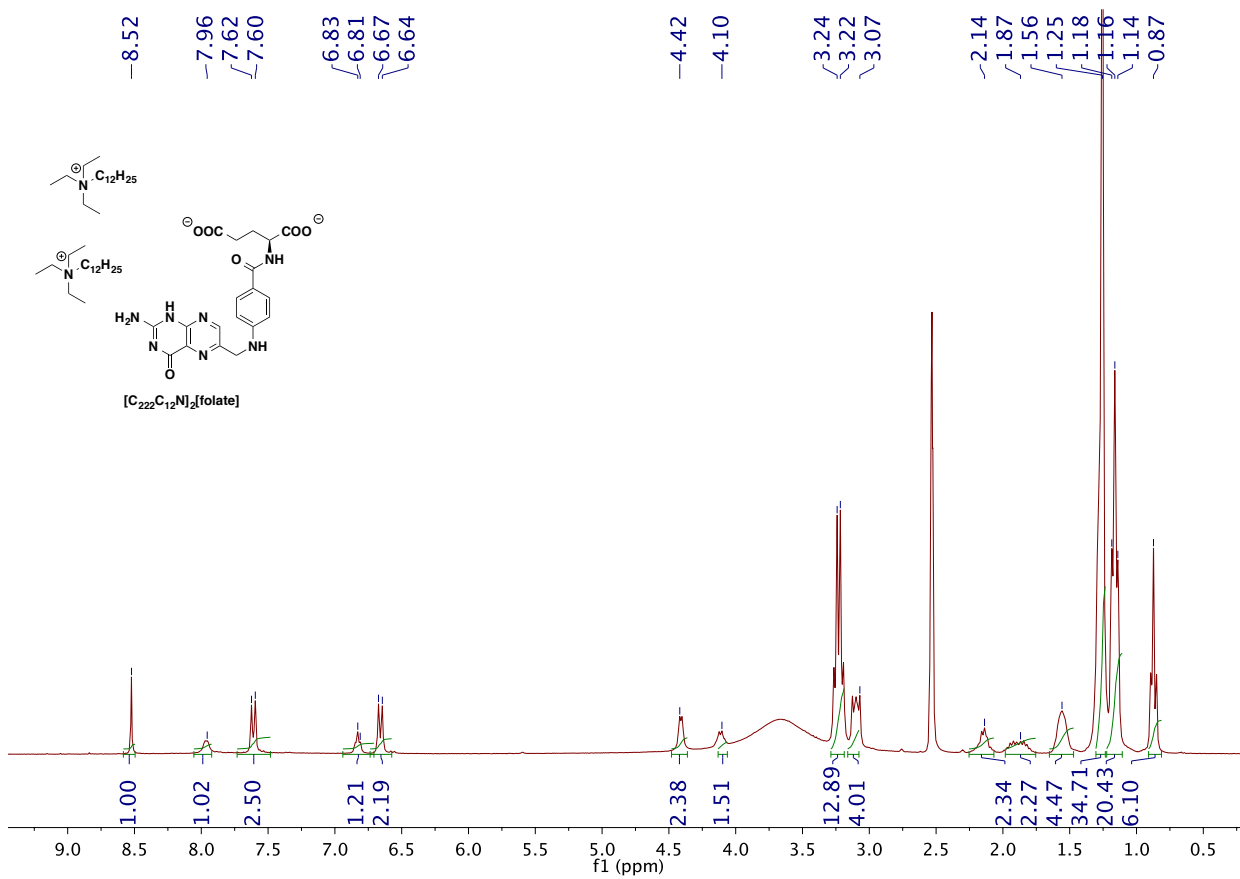


Spectra S1. NMR spectra of  $[\text{Ch}]_2[\text{folate}]$  in  $\text{DMSO-d}_6$ .

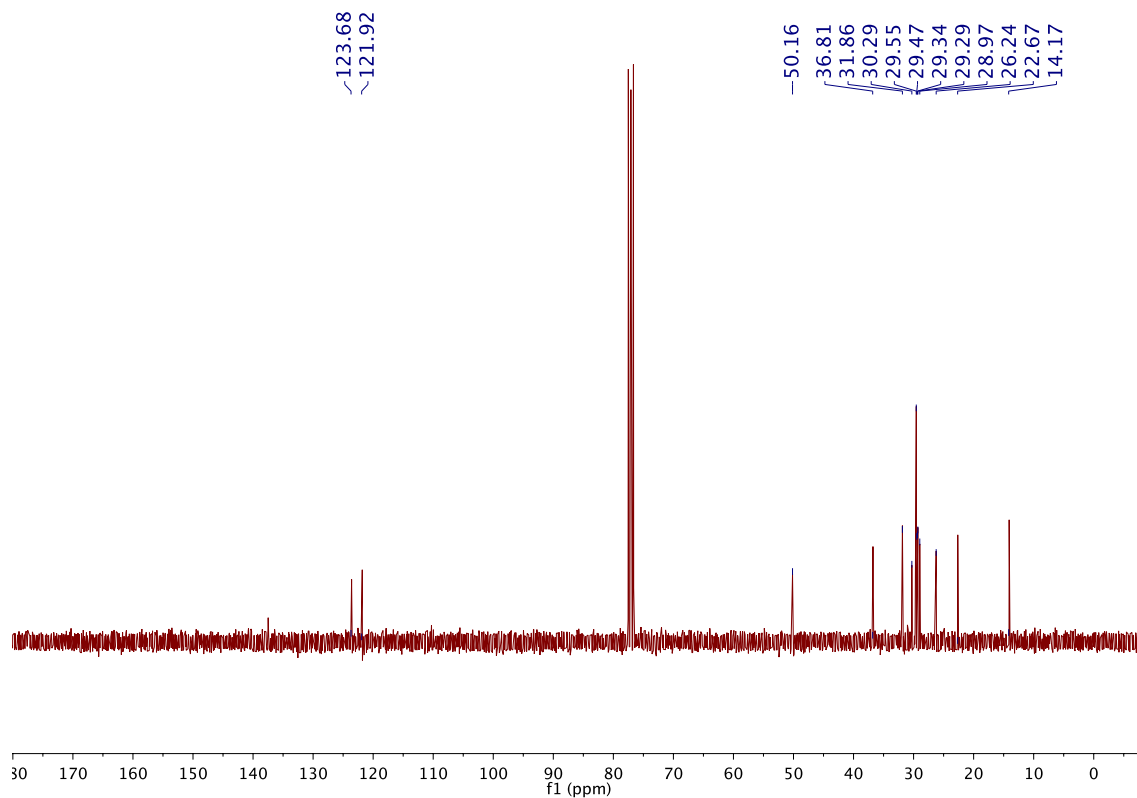
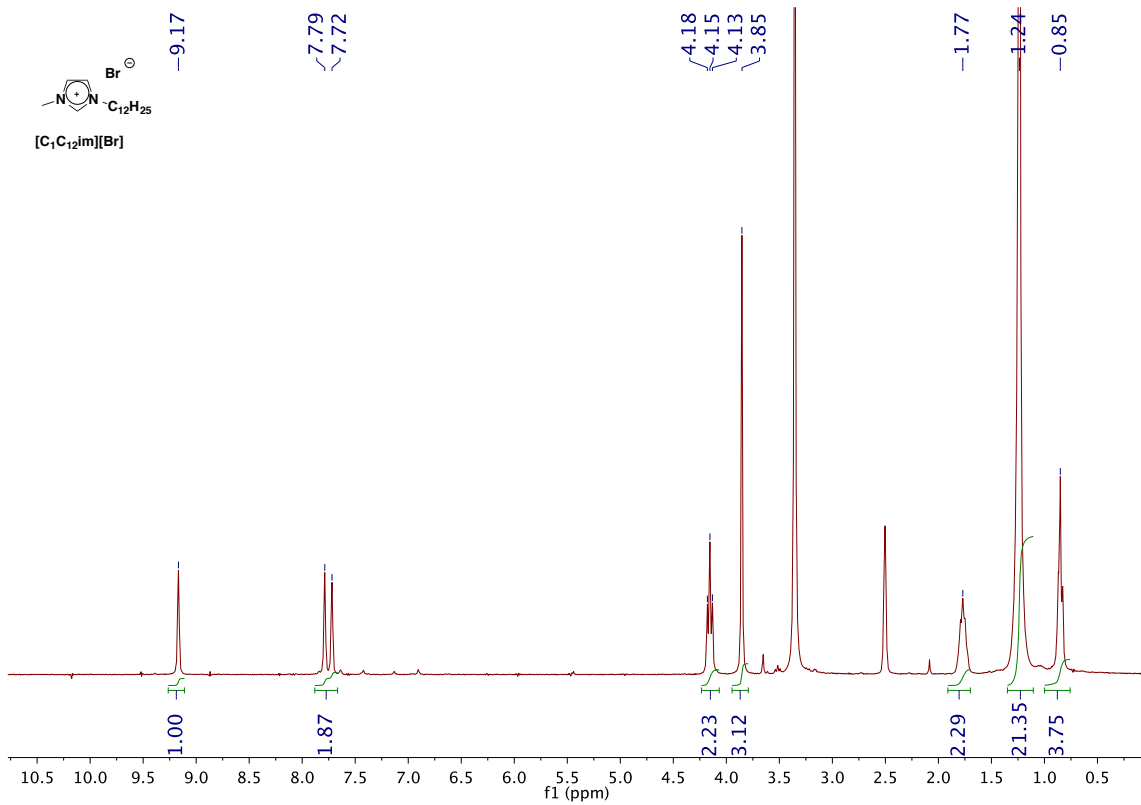




Spectra S2. NMR spectra of  $[\text{C}_{222}\text{C}_{12}\text{N}]_2\text{[Br]}$  in  $\text{CDCl}_3$ .



Spectra S3. NMR spectra of  $[C_{222}C_{12}N]_2[folate]$  in DMSO- $d_6$ .



Spectra S4. NMR spectra of [C<sub>1</sub>C<sub>12</sub>im][Br] in DMSO-d<sub>6</sub>.



**Table S1.** UV-vis values of folate-salts ( $1 \cdot 10^{-4} \text{M}$ ) solution in PBS in presence of BSA at 2 and 40  $\mu\text{M}$ .

	$\lambda$ (nm)	Abs
<b>BSA (2<math>\mu\text{M}</math>)</b>	277	0.0468
<b>BSA (40<math>\mu\text{M}</math>)</b>	277	0.3324
<b>[Ch]<sub>2</sub> [Folate]</b>	364	0.2169
<b>[Ch]<sub>2</sub> [Folate] + BSA (2<math>\mu\text{M}</math>)</b>	359 (max)	0.1317
	364	0.1284
<b>[Ch]<sub>2</sub> [Folate] + BSA (40<math>\mu\text{M}</math>)</b>	351(max)	0.1417
	364	0.1352
<b>[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub> [Folate]</b>	356	0.1445
<b>[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub> [Folate] + BSA (2<math>\mu\text{M}</math>)</b>	351 (max)	0.1603
	356	0.1562
<b>[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub> [Folate] + BSA (40<math>\mu\text{M}</math>)</b>	346 (max)	0.3429
	356	0.3234
<b>[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub> [Folate]</b>	366	0.1897
<b>[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub> [Folate] + BSA (2<math>\mu\text{M}</math>)</b>	366	0.2007
<b>[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub> [Folate] + BSA (40<math>\mu\text{M}</math>)</b>	365	0.1884

**Table S2.** Fluorescence values of folate-salts ( $1 \cdot 10^{-5}$ M) solution in PBS in presence of BSA at 2 and 40  $\mu$ M.

	$\lambda_{max}$ (nm)	$I$	$\lambda$ (nm)	$I$
<b>BSA (2<math>\mu</math>M)</b>	338	548.194		
<b>BSA (40<math>\mu</math>M)</b>	338	1759.47		
<b>[Ch]<sub>2</sub>[Folate]</b>	350	70.0875	443.2	203.249
<b>[Ch]<sub>2</sub>[Folate] + BSA (2<math>\mu</math>M)</b>	342.2(max)	389.655	442	237.955
	350	376.037		
<b>[Ch]<sub>2</sub>[Folate] + BSA (40<math>\mu</math>M)</b>	337.6(max)	1215.47	/	/
<b>[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub>[Folate]</b>	350	39.4114	442.2	298.942
<b>[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub>[Folate] + BSA (2<math>\mu</math>M)</b>	339.2(max)	274.123	442.2	253.605
	350	253.669		
<b>[C<sub>222</sub>C<sub>12</sub>N]<sub>2</sub>[Folate] + BSA (40<math>\mu</math>M)</b>	339.2	1233.61	/	/
<b>[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate]</b>	350	56.1259	442.2	341.233
<b>[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] + BSA (2<math>\mu</math>M)</b>	341.6(max)	307.155	442.2	322.754
	350	291.555		
<b>[C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] + BSA (40<math>\mu</math>M)</b>	337.4	1213.36	/	/

**Table S3.** Apparent dynamic diameter ( $d_H$ ) and polydispersion index (PDI<sub>DLS</sub>) obtained from DLS measurements of [C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] in buffer and buffer/DMSO solution (0.0001 M).

<b>Solvent</b>	<b><math>d_H</math> (nm)</b>	<b>PDI<sub>DLS</sub></b>
PB	650	0.54
PB/DMSO	750	0.58
PBS	740	0.88
PBS/DMSO	980	0.67
Tris	930	0.67
Tris/DMSO	646	0.72

**Table S4.** Gelation tests.

Solvent	Folic acid		[C <sub>222</sub> C <sub>12</sub> N] <sub>2</sub> [folate]		[Ch] <sub>2</sub> [folate]		[C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate]	
	C(wt%) <sup>b</sup>	App. <sup>c</sup>	C(wt%) <sup>b</sup>	App. <sup>c</sup>	C(wt%) <sup>b</sup>	App. <sup>c</sup>	C(wt%) <sup>b</sup>	App. <sup>c</sup>
H <sub>2</sub> O	0.2-2.0%	<b>I</b>	2.0-3.8%	<b>S</b>	2.6-7.2%	<b>S</b>	0.5-5.4%	<b>I</b>
DMSO	0.9-2.0%	<b>S</b>	2.0%	<b>SC</b>	2.3-4.0%	<b>S</b>	2.0%	<b>SC</b>
H <sub>2</sub> O/DMSO (50/50) <sup>a</sup>	0.1-0.4%	<b>G</b>	/	/	0.2-0.7%	<b>SC</b>	/	/
H <sub>2</sub> O/DMSO (90/10) <sup>a</sup>	0.3-2.3%	<b>PS</b>	2.0-4.1%	<b>S</b>	2.2-4.8%	<b>SC</b>	1.8-4.0%	<b>P</b>
TBS (1x)	0.3-1.1%	<b>S</b>	2.1-2.9%	<b>PG</b>	2.6%	<b>SC</b>	0.5-6.4%	<b>G</b>
TBS (1x)/DMSO (50/50) <sup>a</sup>	0.2-0.5%	<b>S</b>	1.9%	<b>S</b>	2.5-4.2%	<b>S</b>	2.4%	<b>P</b>
TBS (1x)/DMSO (90/10) <sup>a</sup>	/	/	1.9-3.9%	<b>S</b>	/	/	2.2-6.1%	<b>G</b>
PB	1.0 - 2.0%	<b>P</b>	2.0-7.3%	<b>S</b>	3.5-7.1%	<b>S</b>	2.2-6.0%	<b>G</b>
PB/DMSO (50/50) <sup>a</sup>	0.3-0.5%	<b>S</b>	1.9%	<b>SF</b>	2.0-4.0%	<b>S</b>	2.0%	<b>S</b>
PB/DMSO (90/10) <sup>a</sup>	/	/	2.0-3.9%	<b>S</b>	/	/	2.3-6.1%	<b>G</b>
PBS (1x)	/	/	4.0%	<b>S</b>	3.9%	<b>S</b>	4.1-5.9%	<b>G</b>
PBS (1x)/DMSO (90/10) <sup>a</sup>	/	/	3.7%	<b>S</b>	3.8%	<b>SC</b>	5.0-6.0%	<b>G</b>
PBS (10x)	0.2-0.3%	<b>P</b>	2.1-6.9%	<b>PG</b>	1.9-9.5%	<b>SC</b>	0.5-4.9%	<b>I</b>
PBS (10x)/DMSO (50/50) <sup>a</sup>	0.2-0.7%	<b>P</b>	1.9-4.8%	<b>P</b>	1.8-4.4%	<b>S</b>	2.0%	<b>P</b>
PBS (10x)/DMSO (90/10) <sup>a</sup>	0.2%	<b>S</b>	2.0-4.0%	<b>S</b>	/	/	2.2-4.0%	<b>I</b>
Ethanol	0.1-2.2%	<b>I</b>	2.0%	<b>S</b>	0.2-2.5%	<b>I</b>	2.0%	<b>S</b>
H <sub>2</sub> O/Ethanol (50/50) <sup>a</sup>	0.2%	<b>S</b>	2.3-4.8%	<b>S</b>	0.2%	<b>SC</b>	2.1-4.0%	<b>P</b>
Glycerol	0.2 -2.0%	<b>P</b>	2.0-6.6%	<b>S</b>	2.9-6.7%	<b>PG</b>	2.0-4.0%	<b>PG</b>
Dioxolane	0.4%	<b>P</b>	/	/	2.3%	<b>I</b>	/	/
1,3-Propanediol	0.2%	<b>I</b>	/	/	2.0-8.4%	<b>S</b>	/	/

<sup>a</sup> volume ratio (v/v); <sup>b</sup>C=concentration range analyzed (g gelator/g solution); <sup>c</sup>App. = appearance: **I** (insoluble), **G** (gel), **PG** (partial gel), **PS** (partially soluble), **P** (precipitate), **SC** (soluble at room temperature), **S** (soluble after heating and cooling of solution).

**Table S5.** I<sub>RLS</sub> at 470 nm for [C<sub>1</sub>C<sub>12</sub>Im]<sub>2</sub>[Folate] gel phases formed in buffer and buffer/DMSO binary mixtures.

gels	I <sub>470 nm</sub>
[C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate] in PB	2160
[C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate] in PB/DMSO 90/10	890
[C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate] in PBS	9370
C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate] in PBS	5680
[C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate] in TBS	840
[C <sub>1</sub> C <sub>12</sub> Im] <sub>2</sub> [folate] in TBS/DMSO	75

## References

1. F. Menges, *Spectragryph- optical spectroscopy software -Version 1.2.16.1*