Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Use of a bis-1,2,3-triazole gelator for the preparation of supramolecular metallogels and stabilization of gold nanoparticles

Markus Tautz,[a] César Saldías,[b] Antonio Diego Lozano-Gorrín[c,d] and David Díaz Díaz*[a,e]

[a] *Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany.*
E-mail: David.Diaz@chemie.uni-regensburg.de
[b] *Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 302, Correo 22, Santiago, Chile*
[c] *Departamento de Química, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain.*
[d] *Instituto Universitario de Materiales y Nanotecnología (IMN), Universidad de La Laguna, 38200 La Laguna, Tenerife, Spain*
[e] *Instituto de Productos Naturales y Agrobiología del CSIC, Avda. Astrofísico Francisco Sánchez 3, 38206 La Laguna, Tenerife, Spain*
E-mail: d.diaz.diaz@ipna.csic.es

Contents List

Contents List

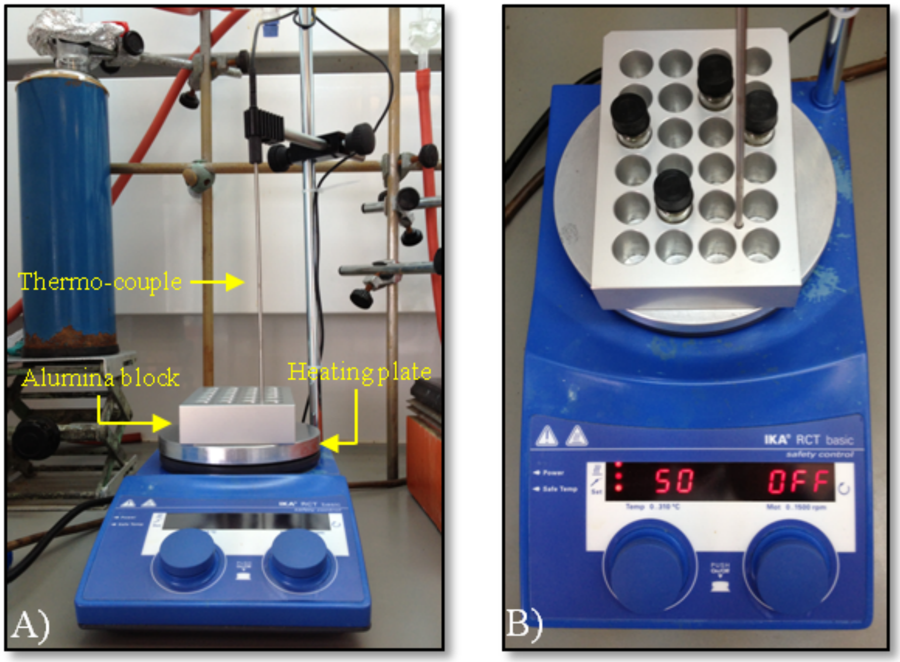


Fig. S1 Custom made set-up for T_{gel} determination. A) Front view showing the composition between electric heating plate, alumina block and digital thermo-couple. B) Top view of the set-up during experimentation containing vials (4 cm length × 1 cm diameter) with gel materials. It is important to mention that the alumina block was constructed especially for one type of vials, which fit smoothly inside the molds to ensure a good transmission of the heat-flow. Verification of the independence of the position inside the custom made apparatus was also performed.

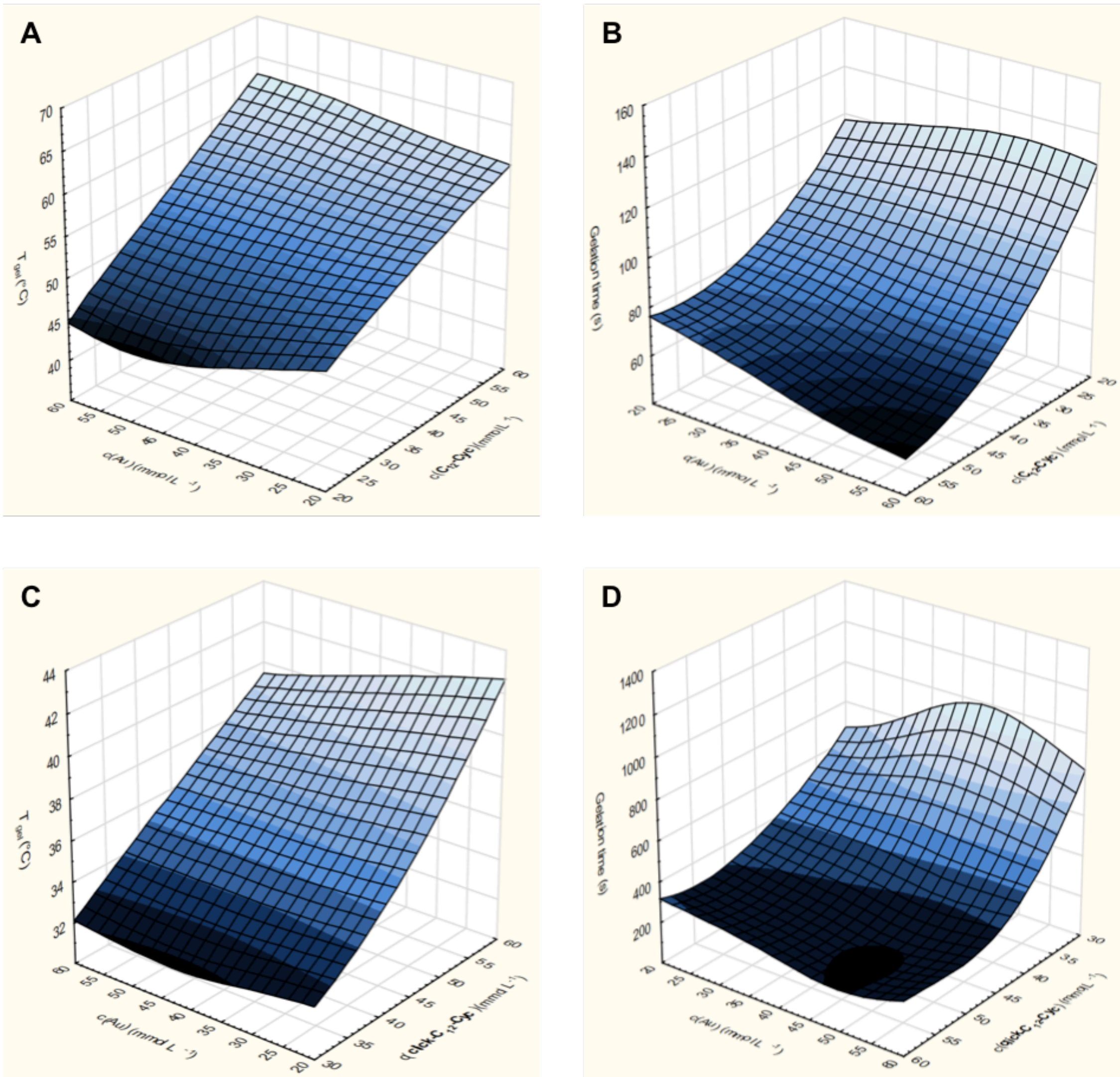


Fig. S2 *Top*: Plots of T_{gel} (A) and gelation time (B) *vs* concentrations of gelator **C_{12}-Cyc** and gold in DMF. *Bottom*: Plots of T_{gel} (C) and gelation time (D) *vs* concentrations of gelator **click-C_{12}-Cyc** and gold in DMF. Note: $HAuCl_4 \cdot 3H_2O$ was found to be hardly soluble in nonpolar solvents and reasonably soluble in NMP, nitromethane, diethyl ether, acetone, DMF, DMSO, ethanol, propan-2-ol, THF and methanol.

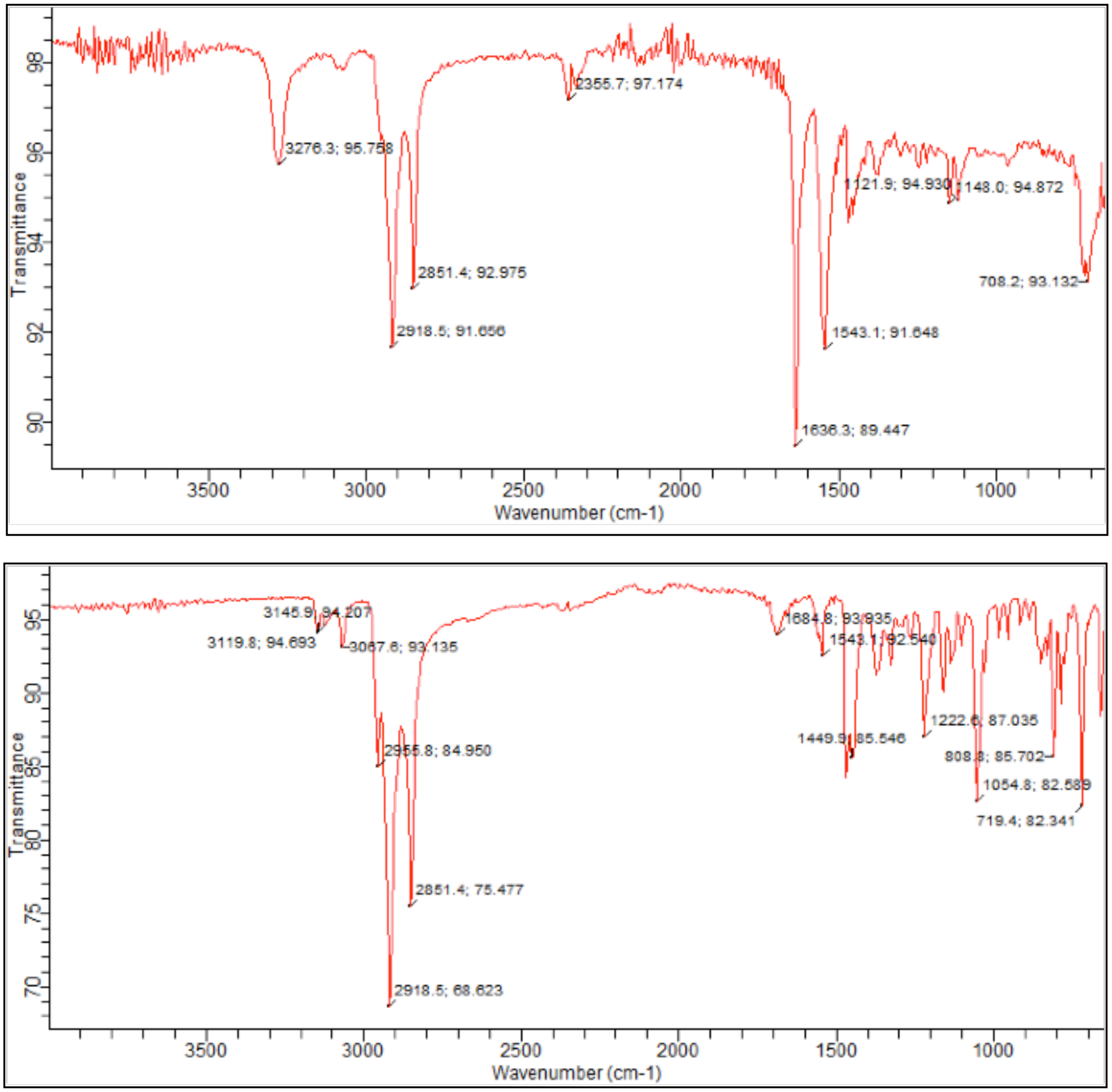
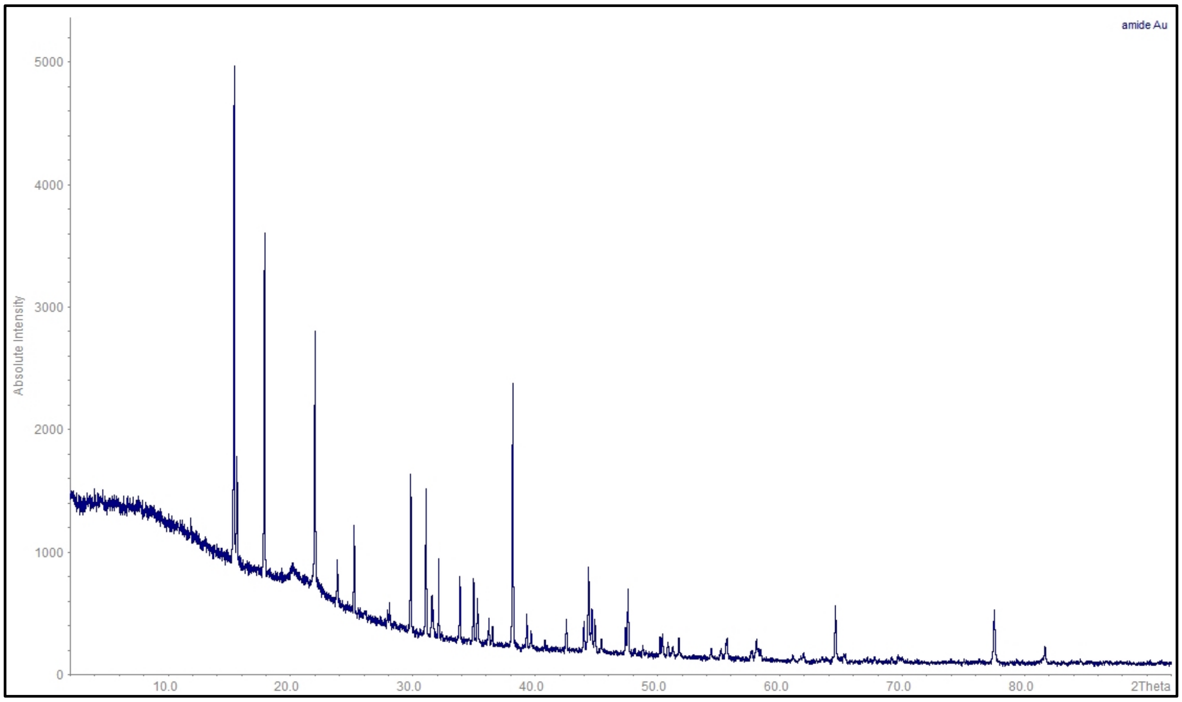


Fig. S3 FT-IR spectra of the metallo-xerogels obtained from **C_{12}-Cyc** (*top*) and **click-C_{12}-Cyc** (*bottom*) incorporating $HAuCl_4{\cdot}3H_2O$ (molar ratio gelator:metal = 1:1; c = 40 mmol L^{-1}) in DMF.



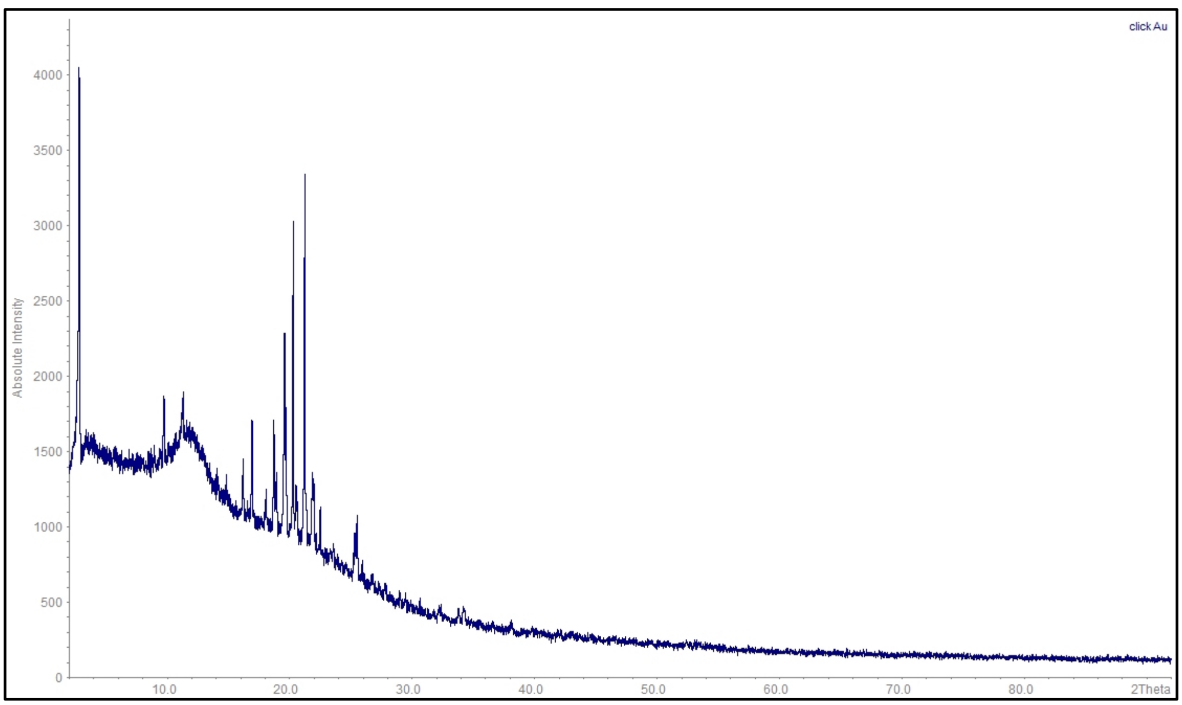


Fig. S4 PXRD spectrum of **C_{12}-Cyc** (*top*) and **click-C_{12}-Cyc** (*bottom*) xerogel incorporating $HAuCl_4 \cdot 3H_2O$ in DMF.

Fig. S5 Response of metallogels prepared from **C_{12}-Cyc** (*left*) and **click-C_{12}-Cyc** (*right*) in DMF to UV light irradiation at 254 nm for 6 h.

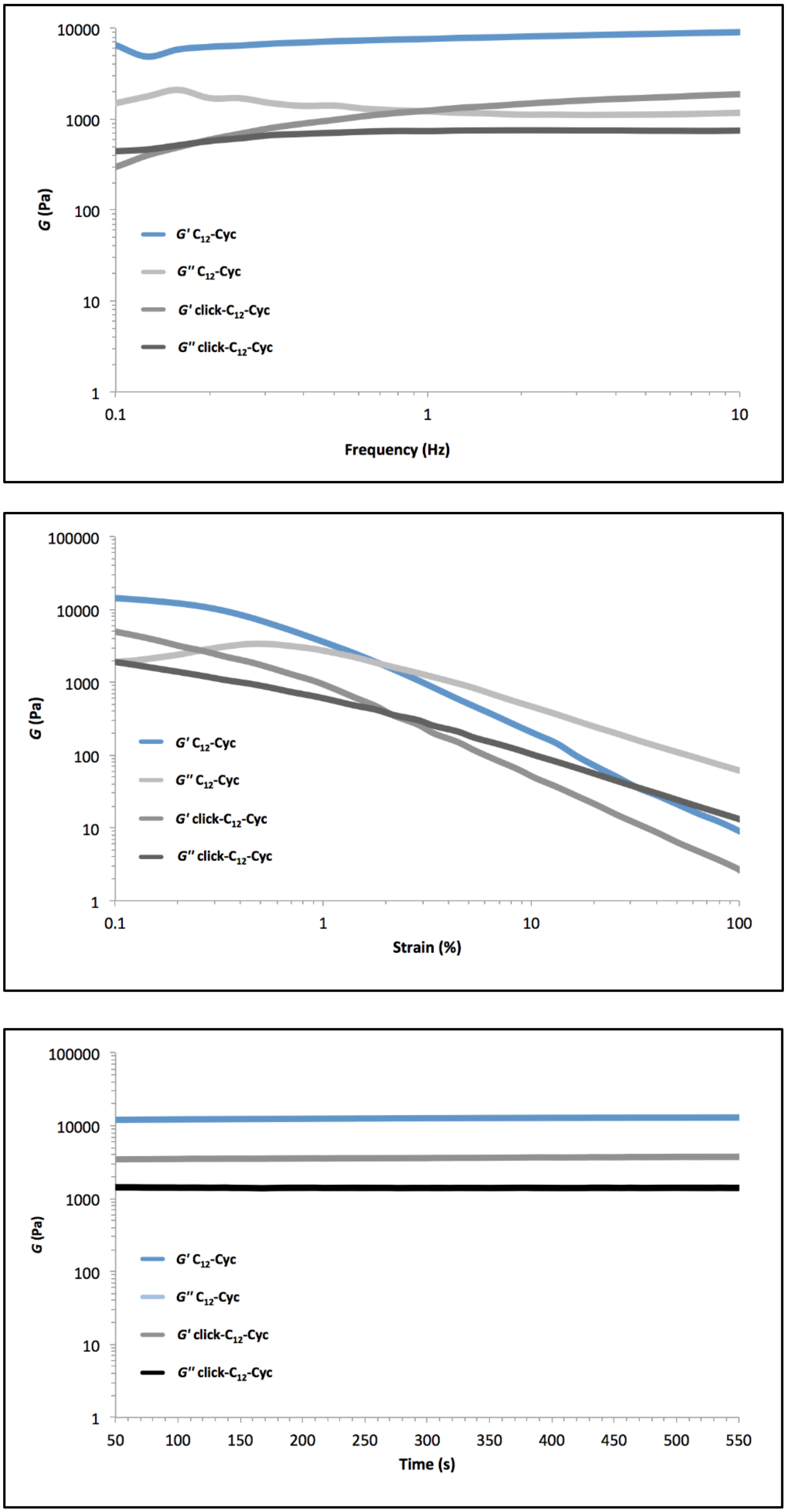


Fig. S6 Oscillatory rheological experiments of gels prepared from **C_{12}-Cyc** and **click-C_{12}-Cyc** in DMF (c = 40 g L^{-1}) incorporating $HAuCl_4 \cdot 3H_2O$. *Top*: DFS-plots. *Middle*: DSS-plots. *Bottom*: DTS-Plots. Note: Although it is not visible in the plot, *G''* data are located under the *G''* data of **click-C_{12}-Cyc**.

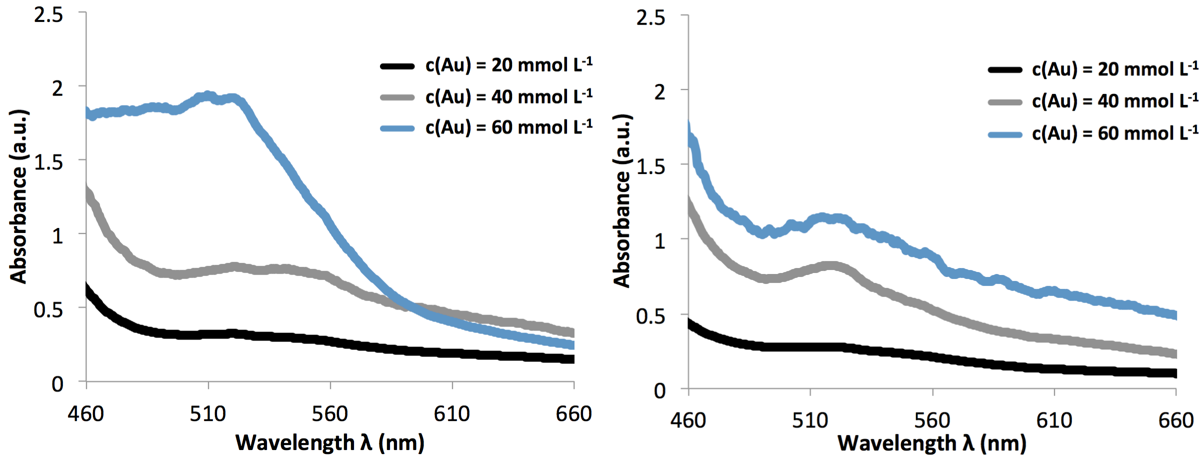


Fig. S7 UV-Vis spectra of gold nanoparticles dispersed in gels prepared from **C_{12}-Cyc** (c = 20 mmol L^{-1}) (*left*) and **click-C_{12}-Cyc** (c = 20 mmol L^{-1}) (*right*). Gels were suspended in DCM. Note 1: For [Au] = 40 mmol L^{-1}, the plasmon band was even more pronounced for the gel made of **click-C_{12}-Cyc**. Note 2: Both gelators showed the same resonance bands as the corresponding raw gelator compounds. This suggested that the intermolecular interactions and the aggregation patterns remained similar when incorporating $HAuCl_4{\cdot}3H_2O$ into the network. In addition, xerogel formation from DMF was found to maintain a high degree of order inside the network as indicated by the crystalline behavior observed by XRD spectroscopy.

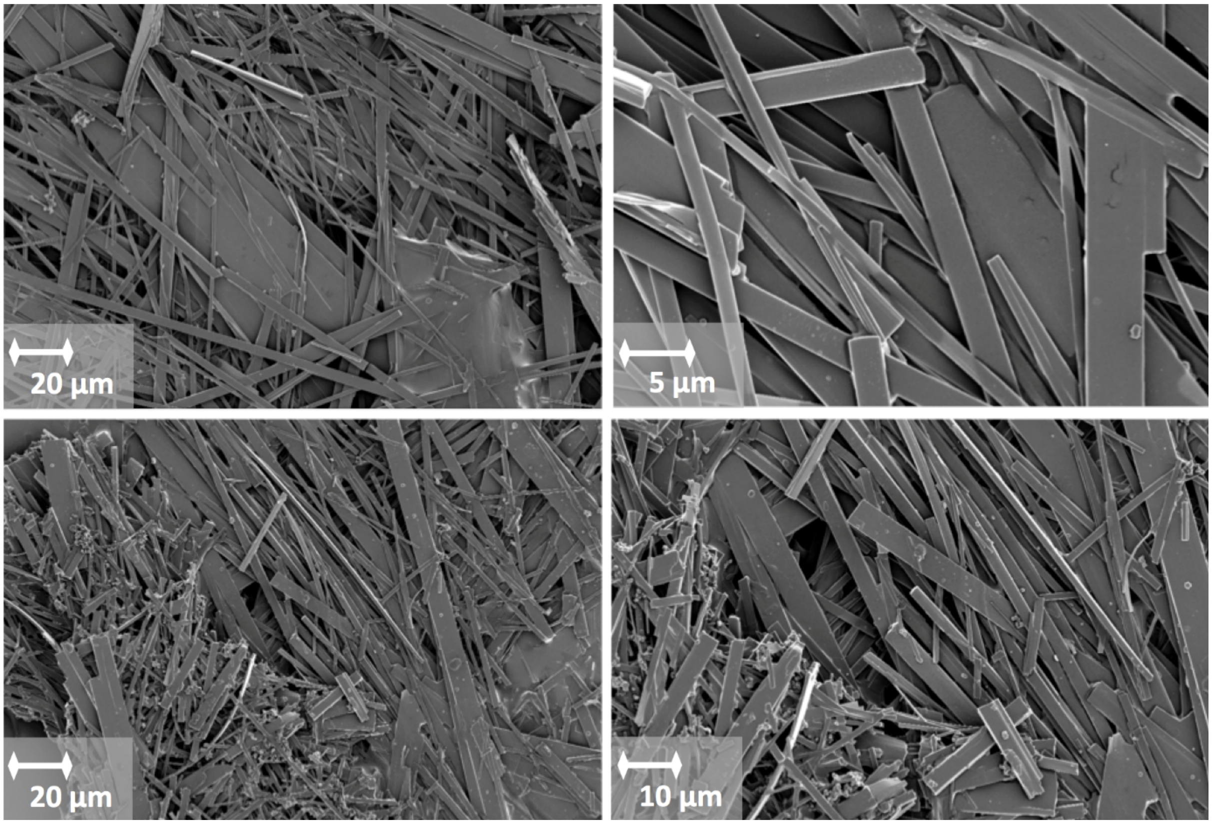


Fig. S8 Additional FESEM pictures of a xerogel prepared from **click-C_{12}-Cyc** (c = 40 mmol L^{-1}) with $HAuCl_4 \cdot 3H_2O$ (c = 40 mmol L^{-1}) and Et_3N (c = 400 mmol L^{-1}) in DMF.

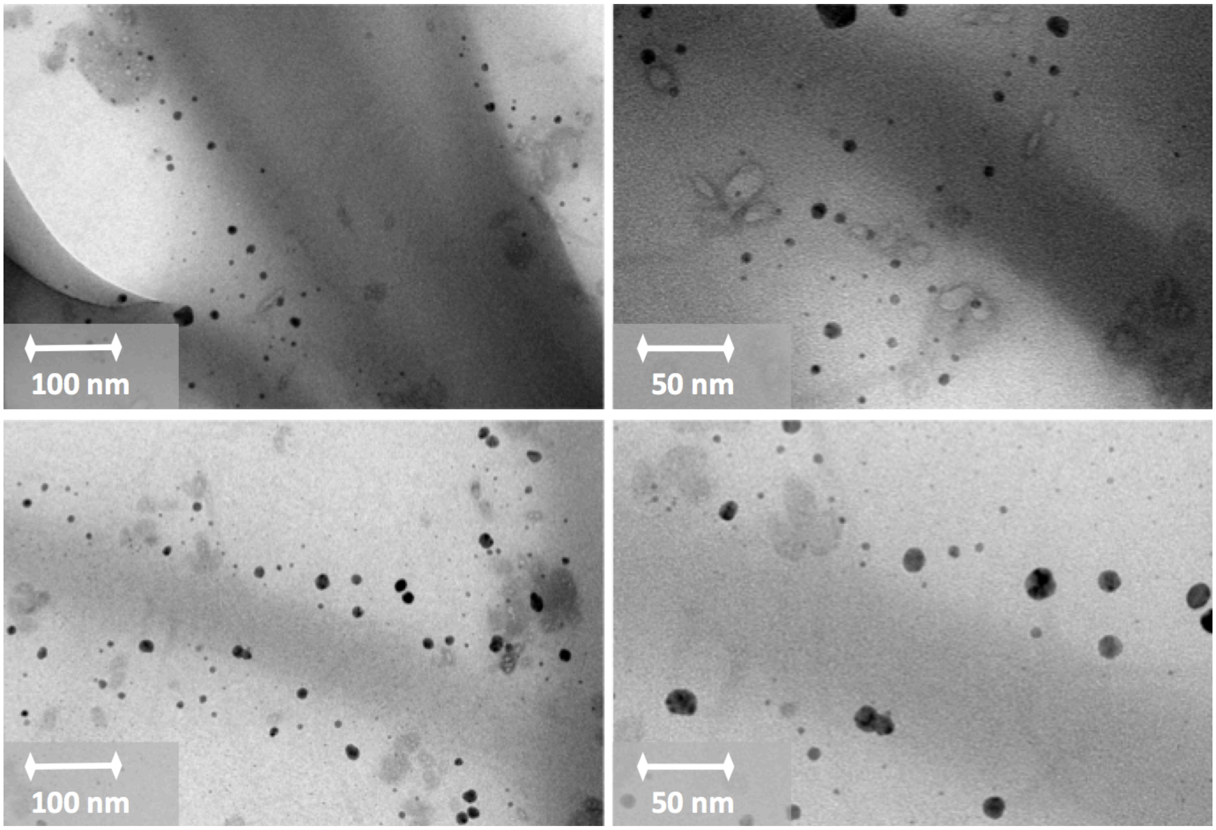


Fig. S9 Additional TEM pictures of a gel prepared from **C_{12}-Cyc** (c = 40 mmol L^{-1}) with $HAuCl_4 \cdot 3H_2O$ (c = 40 mmol L^{-1}) and Et_3N (c = 400 mmol L^{-1}) in DMF.

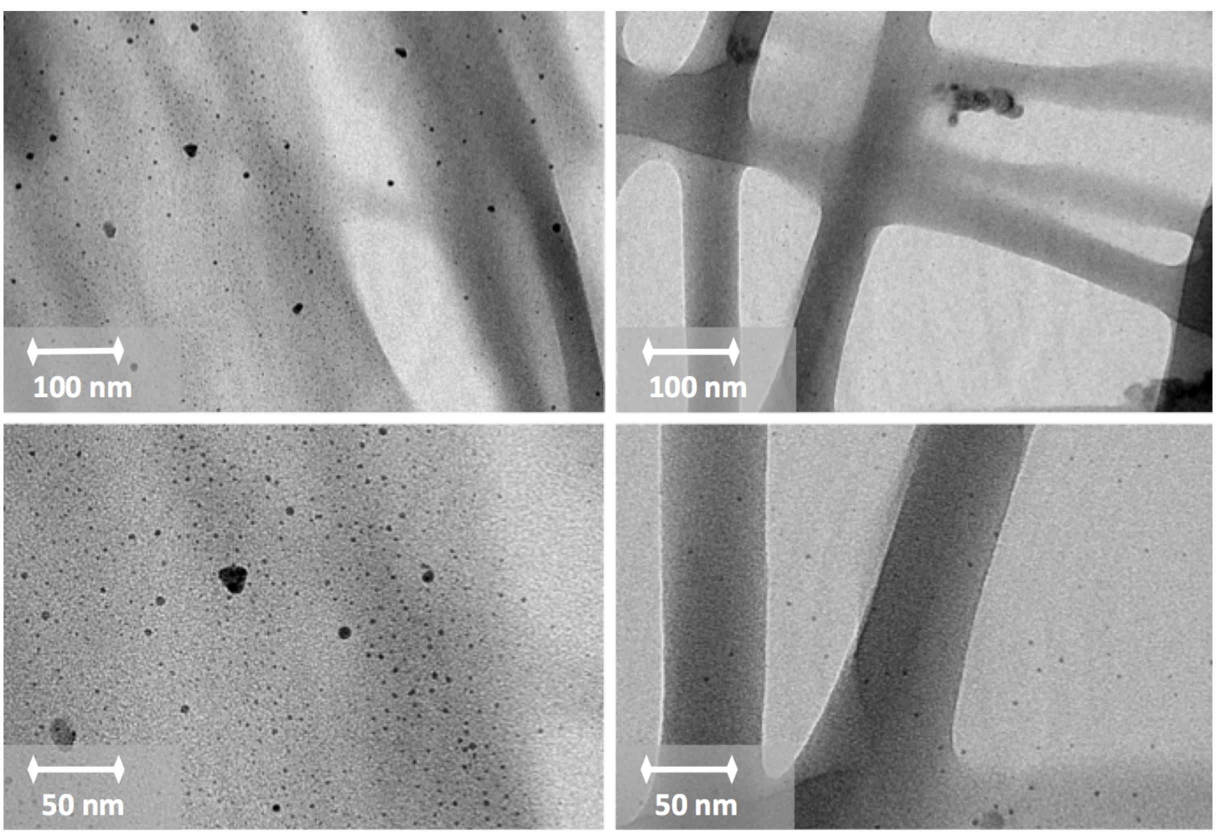


Fig. S10 Additional TEM pictures of a gel prepared from **C_{12}-Cyc** (c = 20 mmol L^{-1}) and **click-C_{12}-Cyc** (c = 20 mmol L^{-1}) with $HAuCl_4 \cdot 3H_2O$ (c = 40 mmol L^{-1}) and Et_3N (c = 400 mmol L^{-1}) in DMF.

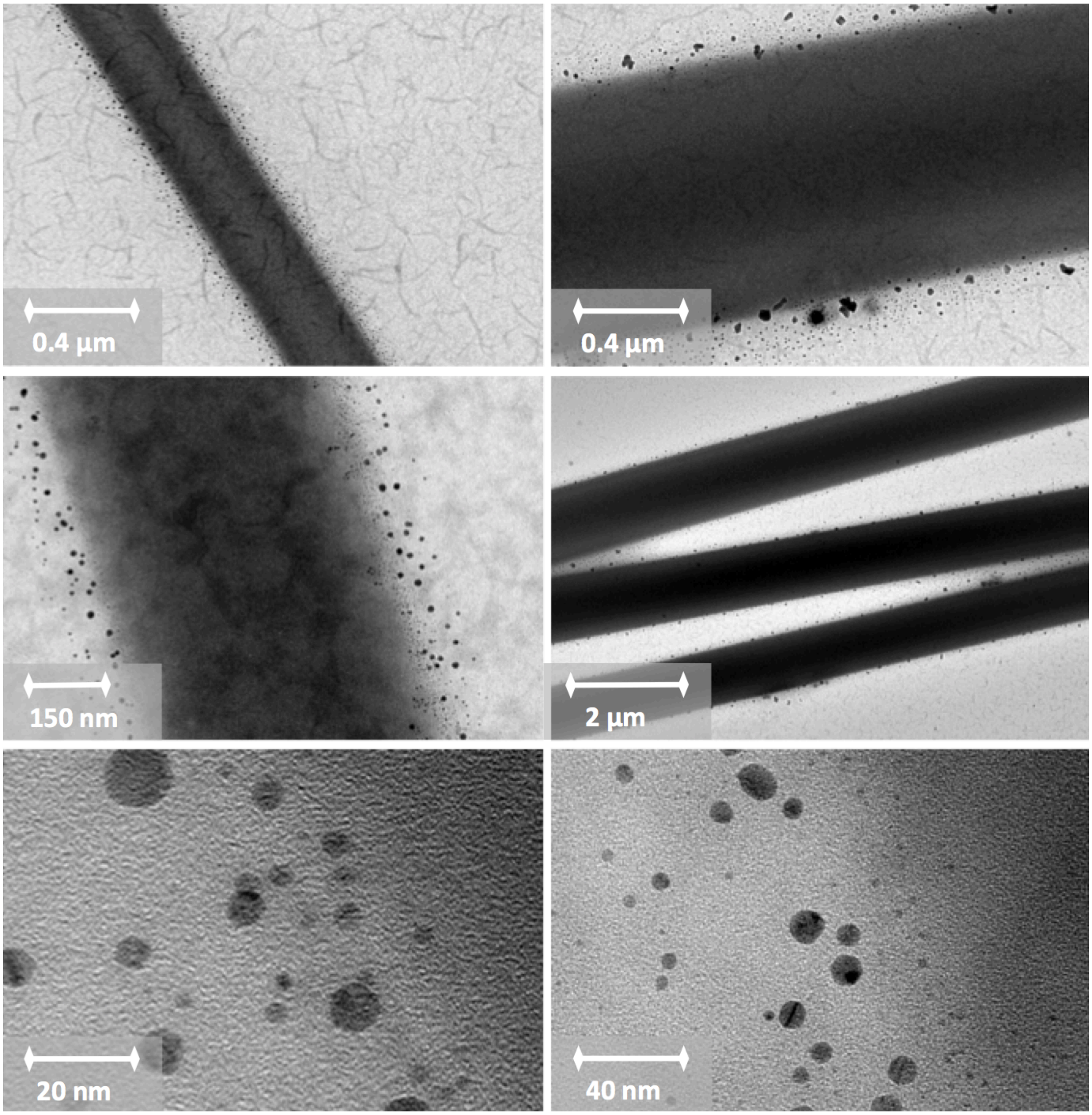


Fig. S11 Additional TEM pictures of a gel prepared from **click-C$_{12}$-Cyc** (c = 40 mmol L^{-1}) with $HAuCl_4·3H_2O$ (c = 40 mmol L^{-1}) and Et_3N (c = 400 mmol L^{-1}) in DMF.

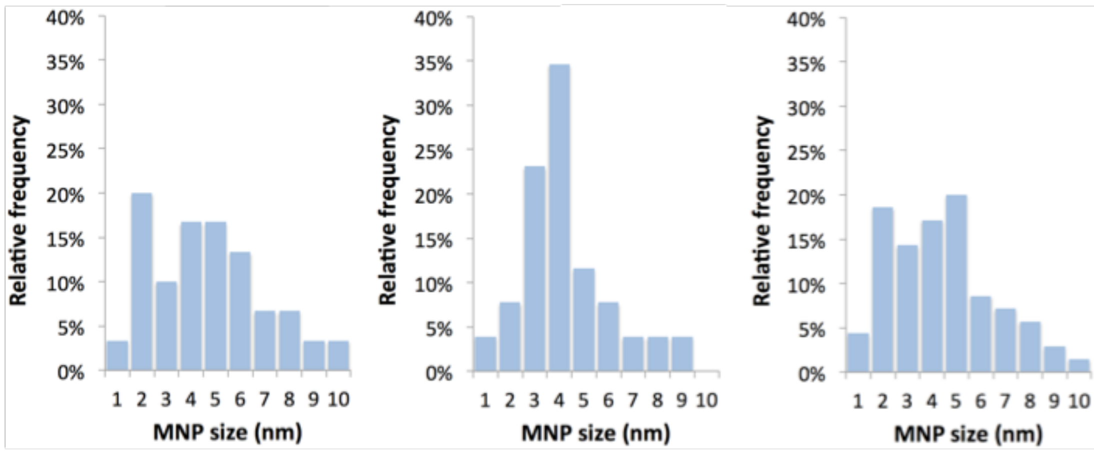


Fig. S12 Nanoparticle size distribution diagrams of gels prepared from **C_{12}-Cyc** (c = 40 mmol L^{-1}) (*left*), **C_{12}-Cyc** and **click-C_{12}-Cyc** (c = 20 mmol L^{-1} (each)) (*middle*) and **click-C_{12}-Cyc** (c = 40 mmol L^{-1}) (*right*) with $HAuCl_4 \cdot 3H_2O$ (c = 40 mmol L^{-1}) and Et_3N (c = 400 mmol L^{-1}) in DMF. Note: The use of DMF as solvent and Et_3N as reducing agent enabled the easy preparation of the xerogels by freeze-drying the corresponding wet gels for 5 h under reduced pressure.

Fig. S13 Appearance of gold NPs-containing xerogel of **click-C_{12}-Cyc**.

Table S1 Screening of gel formation with different mixtures containing **click-C_{12}-Cyc** and 250 µL of solvent in the presence of metal ions.

Entry	Metal salt	Solvent	Preparation	β (**click-C_{12}-Cyc**) / mg mL^{-1}	β (metal) / mg mL^{-1}	c (metal) / mol%	Appear-ance
1	$PdCl_2$	DMSO	heat., sonic.	4,8	2,0	124%	op. sol.
2	$PdCl_2$	DMF	heat., sonic.	5,6	1,6	85%	cl. sol.
3	$Cu(OAc)_2{\cdot}H_2O$	DMSO	heat., sonic.	6,4	2,8	115%	op. sol.
4	$Cu(OAc)_2{\cdot}H_2O$	DMF	heat., sonic.	4,8	1,6	88%	cl. sol.
5	$Co(OAc)_2{\cdot}4H_2O$	DMSO	heat., sonic.	4,8	2,0	88%	op. sol.
6	$Co(OAc)_2{\cdot}4H_2O$	DMF	heat., sonic.	5,6	2,0	76%	cl. sol.
7	$CoCl_2{\cdot}6H_2O$	DMSO	heat, son.	4,4	2,4	121%	op. sol.
8	$CoCl_2{\cdot}6H_2O$	DMF	heat., sonic.	4,4	2,0	101%	cl. sol.
9	$NiCl_2{\cdot}6H_2O$	DMSO	heat., sonic.	5,2	2,0	85%	op. sol.
10	$NiCl_2{\cdot}6H_2O$	DMF	heat., sonic.	5,6	2,4	95%	cl. sol.
11	-	DMSO	heat., sonic.	5,2	-	-	op. sol.
12	-	DMF	heat., sonic.	5,2	-	-	cl. sol.
13	$PdCl_2$	DMSO	heat. and cool.	4,8	2,0	124%	op. sol.
14	$PdCl_2$	DMF	heat. and cool.	5,6	1,6	85%	cl. sol.
15	$Cu(OAc)_2{\cdot}H_2O$	DMSO	heat. and cool.	6,4	2,8	115%	op. sol.
16	$Cu(OAc)_2{\cdot}H_2O$	DMF	heat. and cool.	4,8	1,6	88%	cl. sol.
17	$Co(OAc)_2{\cdot}4H_2O$	DMSO	heat. and cool.	4,8	2,0	88%	op. sol.
18	$Co(OAc)_2{\cdot}4H_2O$	DMF	heat. and cool.	5,6	2,0	76%	cl. sol.
19	$CoCl_2{\cdot}6H_2O$	DMSO	heat. and cool.	4,4	2,4	121%	op. sol.
20	$CoCl_2{\cdot}6H_2O$	DMF	heat. and cool.	4,4	2,0	101%	cl. sol.

21	$NiCl_2·6H_2O$	DMSO	heat. and cool.	5,2	2,0	85%	op. sol.
22	$NiCl_2·6H_2O$	DMF	heat. and cool.	5,6	2,4	95%	cl. sol.
23	-	DMSO	heat. and cool.	5,2	-	-	op. sol.
24	-	DMF	heat. and cool.	5,2	-	-	cl. sol.
25	$PdCl_2$	DMSO	heat. and cool.	8,8	2,0	68%	susp.
26	$PdCl_2$	DMF	heat. and cool.	10	1,6	48%	cl. sol.
27	$Cu(OAc)_2·H_2O$	DMSO	heat. and cool.	8,4	2,8	88%	susp.
28	$Cu(OAc)_2·H_2O$	DMF	heat. and cool.	7,2	1,6	59%	cl. sol.
29	$Co(OAc)_2·4H_2O$	DMSO	heat. and cool.	9,2	2,0	46%	susp.
30	$Co(OAc)_2·4H_2O$	DMF	heat. and cool.	9,6	2,0	44%	cl. sol.
31	$CoCl_2·6H_2O$	DMSO	heat. and cool.	6,4	2,4	83%	susp.
32	$NiCl_2·6H_2O$	DMSO	heat. and cool.	10	2,0	44%	susp.
33	$NiCl_2·6H_2O$	DMF	heat. and cool.	7,6	2,4	70%	cl. sol.
34	-	DMSO	heat. and cool.	10	-	-	susp.
35	-	DMF	heat. and cool.	5,2	-	-	cl. sol.
36	$PdCl_2$	DMSO	heat. and cool.	12	2,0	48%	gel
37	$PdCl_2$	DMF	heat. and cool.	12	1,6	41%	cl. sol.
38	$Cu(OAc)_2·H_2O$	DMSO	heat. and cool.	13	2,8	56%	susp.
39	$Cu(OAc)_2·H_2O$	DMF	heat. and cool.	10	1,6	41%	cl. sol.
40	$Co(OAc)_2·4H_2O$	DMSO	heat. and cool.	11	2,0	38%	susp.
41	$Co(OAc)_2·4H_2O$	DMF	heat. and cool.	19	2,0	23%	cl. sol.

42	$CoCl_2{\cdot}6H_2O$	DMSO	heat. and cool.	8,4	2,4	63%	susp.
43	$CoCl_2{\cdot}6H_2O$	DMF	heat. and cool.	6,4	2,0	69%	cl. sol.
44	$NiCl_2{\cdot}6H_2O$	DMSO	heat. and cool.	12	2,0	37%	susp.
45	$NiCl_2{\cdot}6H_2O$	DMF	heat. and cool.	9,2	2,4	58%	cl. sol.
46	-	DMSO	heat. and cool.	13	-	-	susp.
47	-	DMF	heat. and cool.	10	-	-	cl. sol.

op. gel = opaque gel; visc. susp. = viscous suspension; prec. = precipitate with clear solution; heat. = heating; cool. = cooling; sonic. = sonication

Table S2 Screening of gel formation with different mixtures containing **C_{12}-Cyc, click-C_{12}-Cyc** and 250 µL of solvent in the presence of gold and platinum salts.

Entry	Metal salt	Solvent	Gelator	Preparation	β (gelator) / mg/mL	β (metal) / mg/mL	c (metal) / mol%	Apearance
1	$HAuCl_4{\cdot}3H_2O$	Cyclohexane	**click-C_{12}-Cyc**	heat. and cool.	15	18,4	177%	clear sol.
2	$HAuCl_4{\cdot}3H_2O$	DMSO	**click-C_{12}-Cyc**	heat. and cool.	16	15,6	146%	op. gel. yellow
3	$HAuCl_4{\cdot}3H_2O$	Cyclohexane	**C_{12}-Cyc**	heat. and cool.	17	11,6	97%	op. gel. yellow
4	$HAuCl_4{\cdot}3H_2O$	DMSO	**C_{12}-Cyc**	heat. and cool.	16	21,6	190%	op. gel. yellow
5	$PdCl_2$	Cyclohexane	**click-C_{12}-Cyc**	heat. and cool.	15	5,6	103%	op. sol.
6	$PdCl_2$	DMSO	**click-C_{12}-Cyc**	heat. and cool.	15	8,0	147%	op. sol.
7	$PdCl_2$	Cyclohexane	**C_{12}-Cyc**	heat. and cool.	15	5,6	99%	op. sol. colorless
8	$PdCl_2$	DMSO	**C_{12}-Cyc**	heat. and cool.	10	3,6	97%	op. sol. dark orange
9	$HAuCl_4{\cdot}3H_2O$	Nitromethane	**C_{12}-Cyc**	heat. and cool.	24	31,6	186%	prec. yellow
10	$HAuCl_4{\cdot}3H_2O$	Nitromethane	**click-C_{12}-Cyc**	heat. and cool.	24	28,8	175%	cl. sol. yellow
11	$HAuCl_4{\cdot}3H_2O$	Diethylether	**C_{12}-Cyc**	heat. and cool.	24	22,0	129%	prec.
12	$HAuCl_4{\cdot}3H_2O$	Acetone	**C_{12}-Cyc**	heat. and cool.	23	22,0	134%	part. gel
13	$HAuCl_4{\cdot}3H_2O$	Ethanol	**C_{12}-Cyc**	heat. and cool.	25	22,8	130%	precipitate
14	$HAuCl_4{\cdot}3H_2O$	Isopropanol	**C_{12}-Cyc**	heat. and cool.	26	18,8	103%	op. gel
15	$HAuCl_4{\cdot}3H_2O$	THF	**C_{12}-Cyc**	heat. and cool.	25	16,8	95%	prec.
16	$HAuCl_4{\cdot}3H_2O$	Isopropanol	**click-C_{12}-Cyc**	heat. and cool.	52	16,4	46%	cl. gel
17	$HAuCl_4{\cdot}3H_2O$	Acetone	**click-C_{12}-Cyc**	heat. and cool.	45	16,4	54%	cl. gel
18	$HAuCl_4{\cdot}3H_2O$	DMF	**C_{12}-Cyc**	heat. and cool.	24	16,8	99%	op. gel
19	$HAuCl_4{\cdot}3H_2O$	DMF	**click-**	heat. and	24	16,4	100%	op. gel

			C_{12}-Cyc	cool.				
20	$HAuCl_4 \cdot 3H_2O$	NMP	**C_{12}-Cyc**	heat. and cool.	24	16,8	99%	op. gel
21	$HAuCl_4 \cdot 3H_2O$	NMP	**click-C_{12}-Cyc**	heat. and cool.	24	16,4	100%	cl. gel

op. gel = opaque gel; cl. gel = clear gel; prec. = precipitate; part. gel = partial gel (partial solution); cl. sol. = clear solution; op. sol. = opaque solution; heat. = heating; cool. = cooling

Table S3 Screening of gel formation and reduction potential with different mixtures containing **C_{12}-Cyc, click-C_{12}-Cyc** and 250 µL of solvent in the presence of $HAuCl_4 \cdot 3\ H_2O$ and reducing agents.

Entry	Solvent	Gelator	Preparation	Reducing agent (RA)	β (gelator) / mg/mL	β (Au) / mg/mL	c (Au) / mol%	β (RA) / mg/mL	c (RA) / mol%	Apearance
1	NMP	**C_{12}-Cyc**	heat, sonic.[a]	NEt_3	26	33,6	160%	4,4	81%	op. gel dark yellow
2	NMP	**click-C_{12}-Cyc**	heat, sonic.[a]	Et_3N	25	16,0	81%	4,4	87%	visc. susp. orange
3	NMP	**C_{12}-Cyc**	heat, sonic.[b]	Hydroquinone	25	15,6	76%	5,6	98%	op. gel red-brown
4	NMP	**click-C_{12}-Cyc**	heat, sonic.[b]	Hydroquinone	24	24,0	124%	5,2	96%	visc. susp. red-brown
5	DMF	**C_{12}-Cyc**	heat, sonic.[a]	Et_3N	26	15,2	71%	5,3	96%	op. gel orange
6	DMF	**click-C_{12}-Cyc**	heat, sonic.[a]	Et_3N	24	18,0	96%	5,3	109%	op. gel yellow
7	DMF	**C_{12}-Cyc**	heat, sonic.[b]	Hydroquinone	24	18,8	97%	8,8	162%	op. gel yellow
8	DMF	**click-C_{12}-Cyc**	heat, sonic.[b]	Hydroquinone	25	15,2	76%	8,4	150%	op. gel yellow
9	DMF	**C_{12}-Cyc**	heat, sonic.	$NaBH_4$	27	22,0	100%	3,6	170%	op. gel black red
10	DMF	**click-C_{12}-Cyc**	heat, sonic.	$NaBH_4$	24	18,0	95%	8,0	438%	prec. black

op. gel = opaque gel; visc. susp. = viscous suspension; prec. = precipitate with clear solution; sonic. = sonication

a) Addition of Et_3N in last position and then application of heat + sonication

b) Addition of hydroquinone in first place and then addition of NMP and application of heat + sonication