

## Electronic Supplementary Information

### Supramolecular hydrogels from cyclic amino acids and application for synthesis of Pt and Ir nanocrystals

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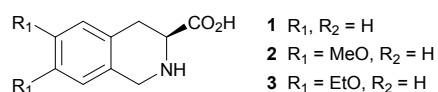
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## General Remarks

Compound **1** was commercial available. Compound **2**·HCl and **3**·HCl were prepared according to literatures.<sup>S1, S2</sup> X-ray single crystallographic analysis was performed with Bruker SMART APEX II CCD diffractometer with graphite-monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal structures were solved by direct methods using the program SHELXL-97 and refined with anisotropic thermal parameters by full matrix least squares on  $F^2$  values with SHELXL-97. TEM and high-resolution TEM (HRTEM) images were taken using a TECNAI G2 high-resolution transmission electron microscope operated at an acceleration voltage of 200 kV. Samples for TEM and HRTEM were prepared by wiping a carbon-coated copper grid on nanoparticles-contained gel followed by natural evaporation of water.



**Scheme S1**

## Water Gelation

*Water gelation tests for 1, 2·HCl and 3·HCl:* To a glass vial containing a hydrogelator (20 mg), was added water (0.4 ml) and heated to form a homogeneous solution at about 80-90 °C. The solution was then cooled to room temperature by standing. After 30 minutes for **1** and **2**·HCl and 2 hours for **3**·HCl at room temperature, if hydrogel was formed as whole, more water (0.1 ml or 0.2 ml) was added to the hydrogel. The heterogeneous suspension was then heated to form a homogeneous solution and cooled to room temperature to check whether a hydrogel formed by inverse tube method. The procedures of water addition, formation of a solution and checking gelation were repeated till no whole gel (partial gelation) was formed, at which the previous weight concentration of the hydrogelator in water was recorded as water gelation concentration.

*Water gelation test for 1·HCl:* To a glass vial containing **1** (16.6 mg, 0.094 mmol), was added 0.5 M aqueous HCl (0.18 ml) and water (0.22 ml) and heated to form a homogeneous solution. After cooling to room temperature, precipitates formed exclusively. Same phenomena was observed for experiment with 0.4 ml of water. **1**·HCl was not able to gel water.

*Water gelation tests for 2 and 3:* To a glass vial containing **2**·HCl (23.1 mg, 0.084 mmol) and NaOH (3.4 mg, 0.084 mmol), was added water (0.4 ml) and heated to form a homogeneous solution at about 80-90 °C. The solution was then cooled to room temperature for gelation. Repeat addition of water and gelation as that for **1**, **2**·HCl and **3**·HCl to obtain water gelation concentration. The compound **3** cannot form hydrogel during the procedure.

According to above experiments, the concentrations for water gelation by weight/weight were 2%, 1%, 1.5% and 2% for **1**, **2**, **2**·HCl and **3**·HCl, respectively.

## Single Crystal Data and Molecular Stacking Therein

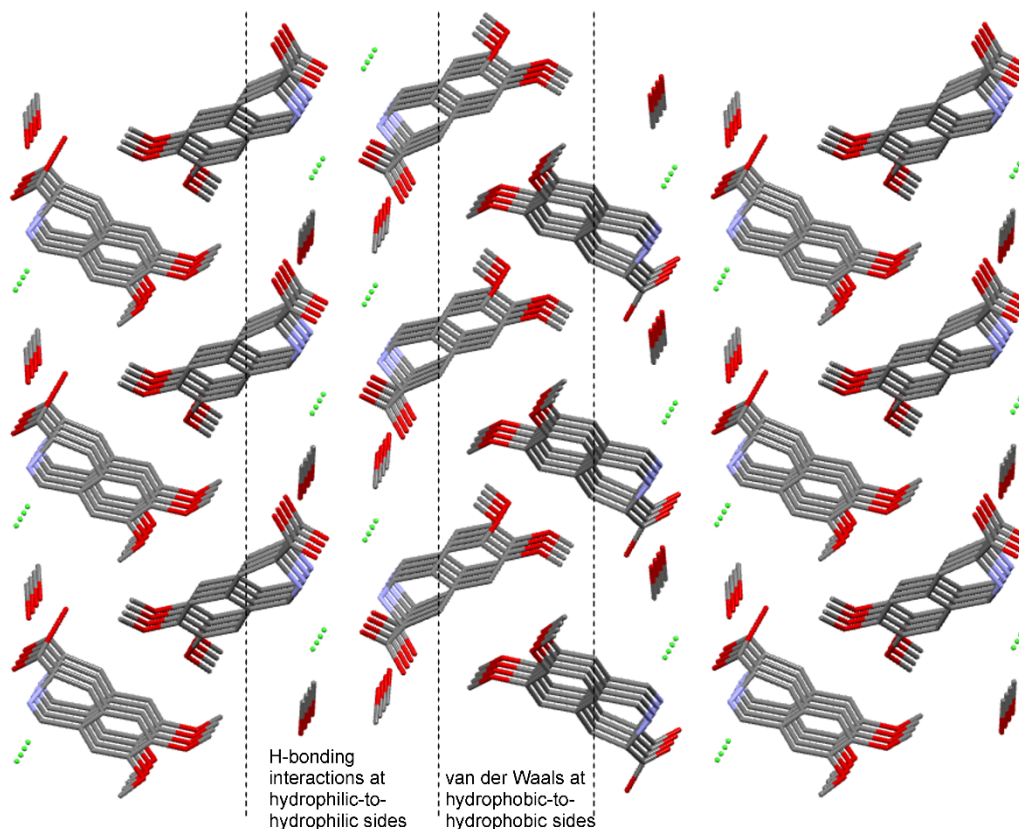
*Crystallization of 2·HCl in methanol:* A methanol solution of **2**·HCl (about 2% wt/vol) was allowed to stand at room temperature. Block granules were formed at the bottom of the solution. The structure information and crystal resolving were listed in Table S1. CCDC number: 843101.

**Table S1.** Single crystal data of 2·HCl·CH<sub>3</sub>OH

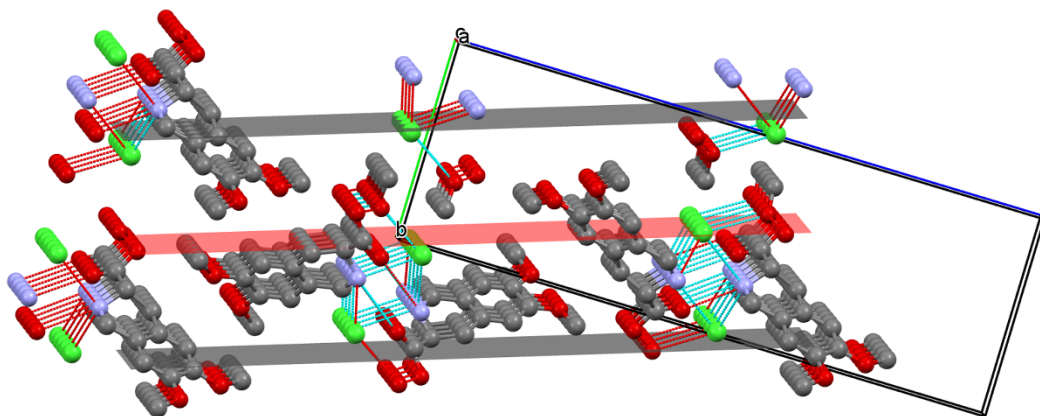
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formula	C <sub>12</sub> H <sub>16</sub> NO <sub>4</sub> ·HCl·CH <sub>4</sub> O
$M_r$	305.75
crystal system	orthorhombic
space group	$P2_12_12_1$
$a$ [Å]	6.2745(4)
$b$ [Å]	9.0192(6)
$c$ [Å]	26.8007(17)
$\alpha$ [°]	90.00
$\beta$ [°]	90.00
$\gamma$ [°]	90.00
$V$ [Å <sup>3</sup> ]	1516.68
$Z$	4
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.339
$\mu$ [mm <sup>-1</sup> ]	0.270
$T$ [K]	296(2)
crystal form	block
crystal size [mm]	0.31x0.26x0.10
crystal color	colorless
absorption correction	multi-scan
total data collected	8060
unique data	2773
observed data [ $I > 2\sigma(I)$ ]	2439
$R_{\text{int}}$	0.0337
$\theta_{\text{max}}$ [°]	25.35
index range	$-6 \leq h \leq 7$ $-10 \leq k \leq 10$ $-32 \leq l \leq 23$
$R_1$ [ $I > 2\sigma(I)$ ]	0.0324
$wR(F^2)$ [ $I > 2\sigma(I)$ ]	0.0742
$R_1$ , all data	0.0698
$wR_2(F^2)$ , all data	0.0777
$S$	1.028
parameters	186

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**Fig. S1.** Hydrophilic-to-hydrophilic and hydrophobic-to-hydrophobic stacking in the single crystal of  $2 \cdot \text{HCl} \cdot \text{CH}_3\text{OH}$ .



**Fig. S2.** The plane (011) of the single crystal of  $2 \cdot \text{HCl} \cdot \text{CH}_3\text{OH}$ , i.e. the space of  $\text{Cl}^-$  ion-containing H-bonds. The green balls represent  $\text{Cl}^-$  ions.

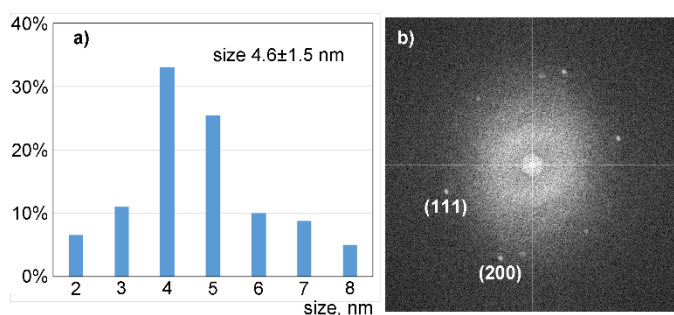
## Synthesis of Pt and Ir Nanocrystals and Characterizations

The synthesis of Pt and Ir nanocrystals were carried out with the hydrogel of  $2 \cdot \text{HCl}$  as matrix. The sizes of nanoparticles were manually measured on two independent TEM images for PtNPs and IrNPs (Fig. S3 and S4). 318 nanoparticles were measured for PtNPs, and 157 nanoparticles were measured for IrNPs. FFT patterns were obtained through Gatan DigitalMicrograph from selected nanocrystals of Pt and Ir NPs (Fig. S5). The hydrogel of  $3 \cdot \text{HCl}$  was also suitable for synthesis of Ir NPs, but not for Pt NPs. As shown in TEM images (Fig. S6), the Ir NPs from the hydrogel of  $3 \cdot \text{HCl}$

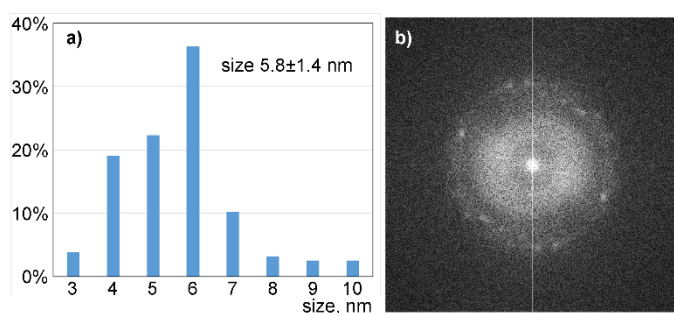
was formed in good crystallinity with size in ranging from 30 – 50 nm, significantly larger than the Ir NPs from the hydrogel of **2**·HCl.

*Synthesis of PtNPs:* An aqueous solution of  $\text{H}_2\text{PtCl}_6$  (20 mM, 0.25 ml) were added to the top of the hydrogel (2%, 1 ml), which was then standing for two days. The upper liquid layer turned almost colorless while the bottom gel layer was coloured. The upper solution was then removed by pipette and the coloured hydrogel (metal ion-contained hydrogel) was placed under hydrogen at 1 atmosphere for 24 hours. The colour of the hydrogel slowly faded to off-white. The PtNPs-hydrogel composite was obtained and characterized with TEM and HRTEM.

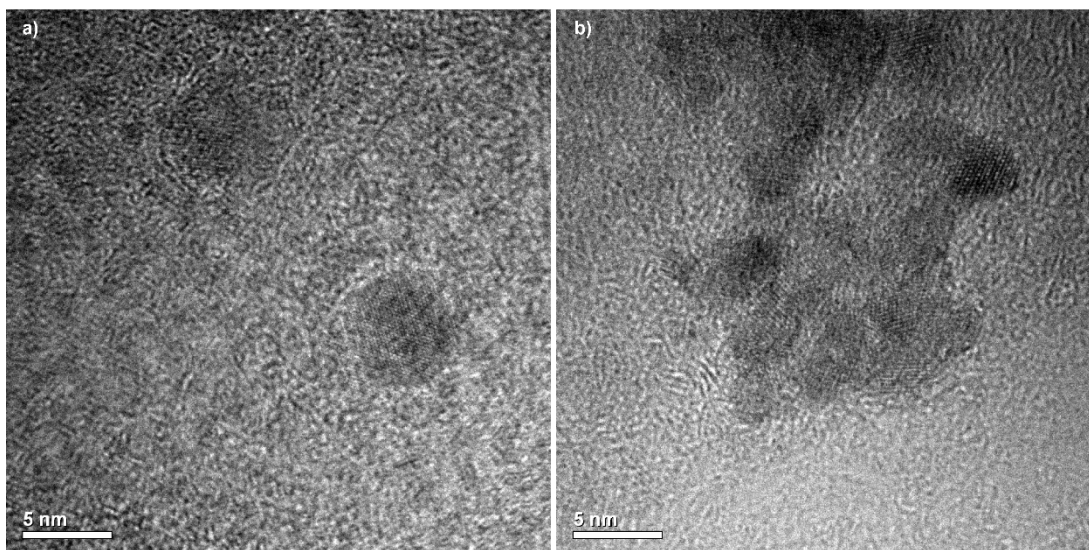
*Synthesis of IrNPs:*<sup>S3</sup> An aqueous solution of  $\text{H}_2\text{PtCl}_6$  (20 mM, 0.25 ml) were added to the top of the hydrogel (2%, 1 ml), which was then standing for two days. The upper liquid layer turned almost colorless while the bottom gel layer was coloured. The upper solution was then removed by pipette. The coloured hydrogel was then covered with aqueous  $\text{NaBH}_4$  (75 mM, 0.25 ml). The colour of the hydrogel slowly faded to off-white within two days. The IrNPs-hydrogel composite was obtained and characterized with TEM and HRTEM.



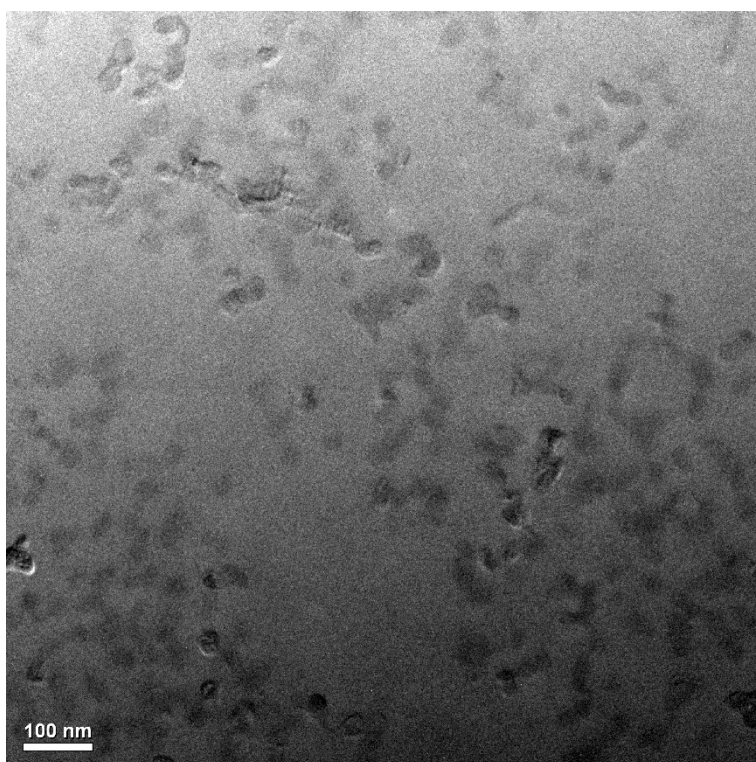
**Fig. S3.** PtNPs: size statistics based on 318 nanoparticles (a), FFT (b) and original nanocrystals for FFT (c)



**Fig. S4.** IrNPs: size statistics based on 157 nanoparticles (a), FFT (b) and original nanocrystals for FFT (c)



**Fig. S5.** Nanocrystals of Pt (a) and Ir (b) for generating the corresponding FFTs



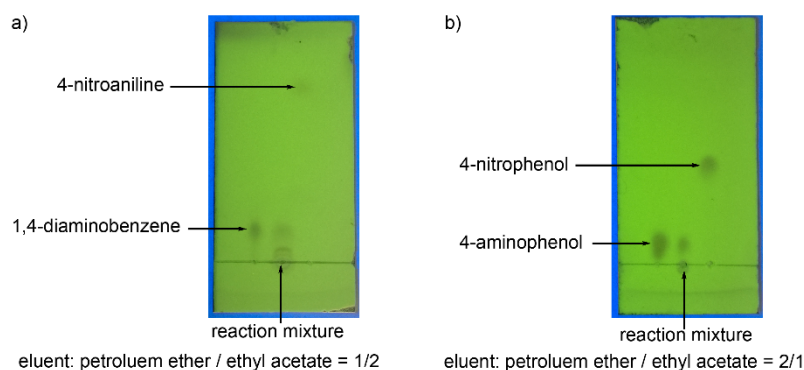
**Fig. S6.** TEM image of Ir NPs from the hydrogel of 3·HCl

## **Catalytic Activity of Pt Nanoparticles**

The catalytic activity of Pt NPs was evaluated with reduction of nitro groups to amino groups with  $\text{NaBH}_4$  as reductant.<sup>S4</sup> The weight ratio of substrate, Pt NPs, and reductant was 5 : 1 : 10, in which the content of Pt NPs in the hydrogel was about 0.25%. Lower  $\text{NaBH}_4$  amount led to partial reduction of the nitro substrates, for which further addition of  $\text{NaBH}_4$  could not lead to completion of the reduction. These results indicated that the catalytic activity of Pt NPs may be lost after long-term

standing in the reaction conditions. The completion of the reduction was checked with TLC by comparison with authentic compounds (Fig. S7) and confirmed with UV-Vis spectra. Besides widely-used 4-nitroaniline, 4-nitrophenol was also successfully reduced. However, Ir NPs did not promote the conversion in our experiments.

*Reduction experiment:* A solution of 4-nitroaniline or 4-nitrophenol (1 ml, 2.5 mg/ml) and NaBH<sub>4</sub> (5 mg) were added to Pt NPs-hydrogel nanocomposites (200 μL, about 0.5 mg of Pt NPs) in a vial at room temperature. The reaction mixture was standing with occasionally vibration. Pt black was formed in the bottom of the vial during the standing. The reaction mixture was monitored with TLC and the completion of the reaction was confirmed with UV-Vis spectra. The nitro substrates 4-nitroaniline or 4-nitrophenol were converted to corresponding 1,4-diaminobenzene or 4-aminophenol within 1 h in quantitative yields.



**Fig. S7.** TLC plates on the completion of the reduction of 4-nitroaniline (a) and 4-nitrophenol (b)

## Reference

- S1. C. Kang, Z. Bian, Y. He, F. Han, X. Qiu, L. Gao, *Chem. Commun.*, 2011, **47**, 10746.
- S2. Z.-X. Wang, S. E. Horne, Brantford Chemicals Inc., US Patent 6642384, 2003, Nov. 4.
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- S4. I. Maity, D. B. Rasale, A. K. Das, *Soft Matter*, 2012, **8**, 5301.