

Electronic Supplementary Information (ESI)

A single-step emulsion approach to prepare fluorescent nanoscale coordination polymers for bioimaging

Zhiyong Sun,^a Yangxue Li,^b Xingang Guan,^b Tingting Sun,^b Li Chen,^{*a} Zhigang Xie,^{*b} and Xiabin Jing^b

Contents

1. Instruments
2. Materials
3. Synthesis
4. Photo images
5. Fluorescent Spectrum of NCPs
6. Microscopic images
7. Supporting references

1. Instruments

The thermogravimetric analysis (TGA) was performed using a Netzsch Sta 449c thermal analyzer system at the heating rate of 10° C/min in air atmosphere. The FTIR spectra were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The nitrogen adsorption isotherm was measured on an Autosorb iQ2 adsorptometer, Quantachrome Instruments. The XRD was performed by a Rigaku D/MAX2550 diffractometer using CuK α radiation, 40 kV, 200 mA with scanning rate of 0.4 ° /min. TEM micrographs was recorded using a FEI Tecnai G2F20 s-twin D573 with an acceleration voltage of 300 kV. SEM micrographs were performing on JEOL JXA- 840 under an accelerating voltage of 15 kV. The ¹H-NMR spectra were recorded at 400 MHz in CDCl₃ and DMSO-d₆ as internal standard with TMS.

2. Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted.

3. Synthesis

3.1 Synthesis of 2,7-(4- methoxycarbonyl -benzene)-9,9'-dioctyl-9H-fluorene

The ligand was synthesized through Suzuki coupling reaction. 274 mg (0.5 mmol) 2,7-Dibromo-9,9-dioctyl-9H-fluorene and 198 mg (1.1 mmol) Methyl 4-boronobenzoate were dissolved in 20 ml Ethylene glycol dimethyl ether and then degassed for 20 minutes in a pressure vessel. Then 1ml (2 M/L) NaHCO₃ was added and then 70 mg Pd(PPh₃)₄ was added. The vessel was then sealed and heated in oil bath at 100 °C for two days¹. After cooled to room temperature, the mixture was diluted with water and extracted with chloroform for two times. Then the organic layer was with anhydrous MgSO₄. After filtered and evaporation, the crude product was purified by silica gel column chromatography (ethyl acetate : petroleum =1:20) to get white powder in a yield of 45%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): (3.88, 6H); (7.53, 2H); (7.56, 2H); (7.66, 4H); (7.73, 2H); (8.06, 4H).

3.2 Synthesis of 2,7-(4-carboxyl-benzene)-9,9'-dioctyl-9H-fluorene

The powder got was dissolved in a mixture of methanol : THF : NaOH (3 M) =1:1:1 in a round bottom , then the

mixture was heated to reflux overnight. After cooled to room temperature, the mixture was extracted with dichloromethane, the up layer was acidification by hydrochloric acid, and white precipitate was seen, then the precipitate was extracted with ethyl acetate. And after evaporation of the solvent, we got the white powder product. $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ (ppm): (7.76, 2H); (7.86, 2H); (7.90, 4H); (7.97, 2H); (8.05, 4H); (12.94, 2H).

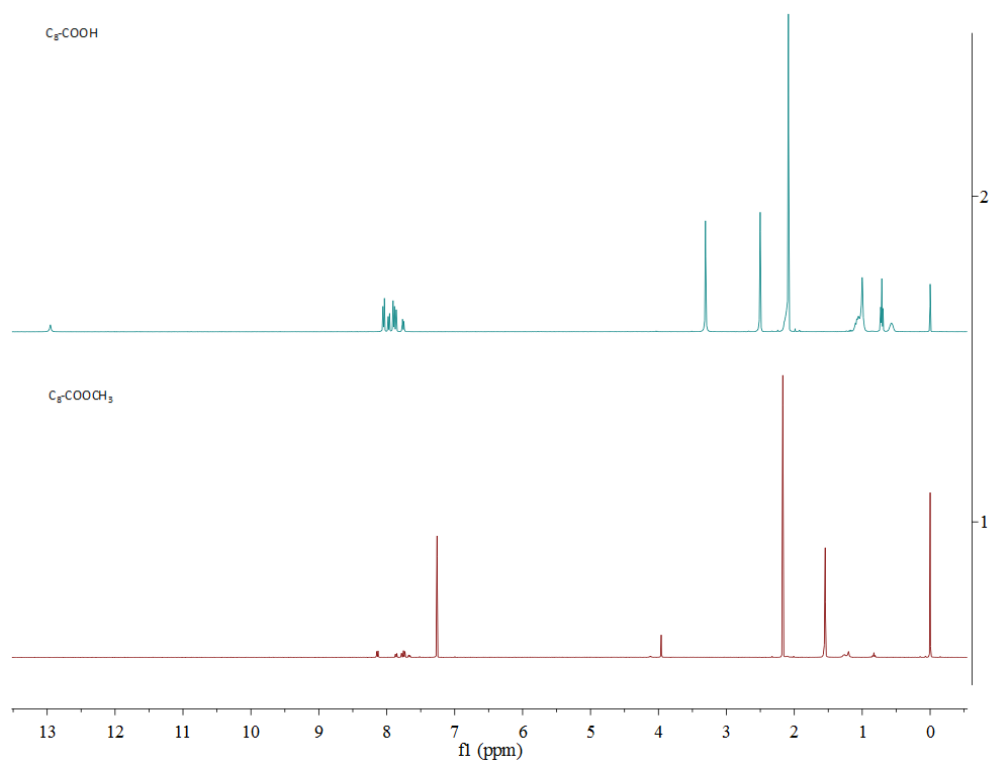


Fig S1. $^1\text{H NMR}$ Spectroscopy (b) of ligand before (red) and after (blue) hydrolysis.

3.3 Synthesis of the nanoscale coordination polymers (NCPs)

The ligand (20 mg) was dissolved in DMF (5 ml) with ZrCl_4 (20 mg), 10ul CF_3COOH and 3 drops of HCl were added for modulation of the crystallinity.² Then the mixture was dropped into a beaker with heated oil at 95 °C by a syringe. ³After 10 minutes reaction, the oil was quickly cooled to room temperature, then the white precipitate was seen at the bottom of the beaker. After centrifugation and washed with DMF and ethanol for several times, then dried in a heated oven at 70 °C, we got the NCPs.

4 Photo images



Fig S2. Photo images of NCPs after dispersed in water with (left) and without (right) a handy UV light.

5 Fluorescent Spectrum of NCPs

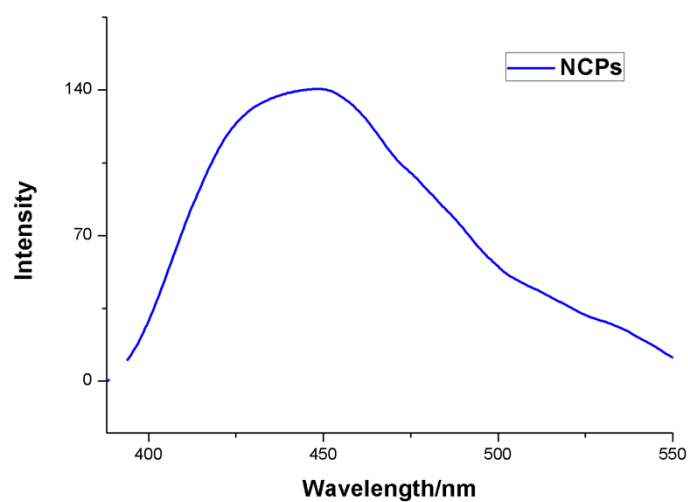


Fig S3 Fluorescent Spectrum of NCPs in water

6 Microscopic images

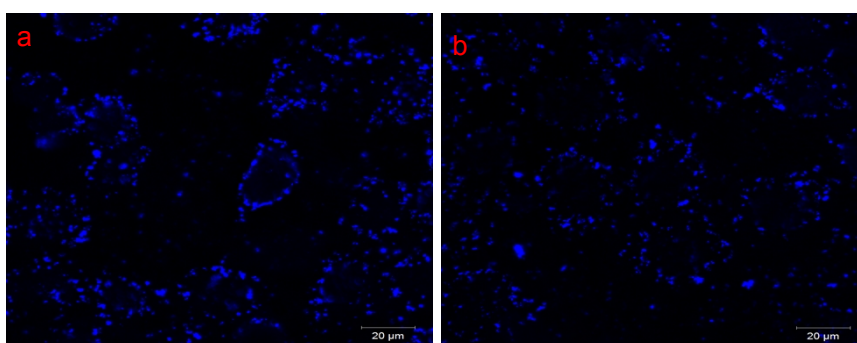


Fig S4. Microscopic images of cells with the ligand as bioimaging agent. The scale bars are 20 μm.

7 Supporting references

1. Ma, J. P.; Yu, Y. and Dong, Y. B., *Chem Commun (Camb)*, 2012, **48**, 2946.
2. Vermoortele, F.; Bueken, B.; Le Bars, G.; Van de Voorde, B.; Vandichel, M.; Houthoofd, K.; Vimont, A.; Daturi, M.; Waroquier, M.; Van Speybroeck, V.; Kirschhock, C. and De Vos, D. E., *J Am Chem Soc*, 2013, **135**, 11465.
3. Faustini, M.; Kim, J.; Jeong, G. Y.; Kim, J. Y.; Moon, H. R.; Ahn, W. S. and Kim, D. P., *J Am Chem Soc*, 2013, **135**, 14619.