

Supporting Information

Tuneable luminescence and morphology of amphiphilic platinum(II) complex via the incorporation of cationic surfactant

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1. Materials and Instruments.

All reagents were used as received and without further purification, or were prepared according to literature procedure. 1, 12-Dibromododecane (95%) and Potassium tert-butoxide (98%) were purchased from J&K, 2-ethoxyethanol and (2, 4-difluorophenyl)boronic acid (98%) were purchased from TCI. The ultrapure water was purified by Aquapro ALH-6000-U.

¹H NMR Experiments

¹H NMR spectra were recorded on a 400 MHz Bruker spectrometer in CDCl₃ solutions, by using Me₄Si as internal standard. Chemical shifts were reported in ppm downfield from Me₄Si.

ESI-MS Experiments

ESI-MS were recorded on a Bruker APEX II Fourier transform ion cyclotron mass spectrometer resonance.

UV-Vis Absorption Spectra Experiments

UV-vis absorption spectra were recorded by using an Agilent Technologies Cary 60 spectrophotometer.

Emission Spectra Experiments

Luminescence measurements were made on Edinburgh Edinburgh FLS920 with a xenon lamp as the excitation source and optical filter. Quantum yield was obtained with Edinburgh FLS920 spectrograph using excitation wavelength at 385 nm.

Fluorescence Microscope Experiments

Fluorescence microscope images were performed with Leica DM4000B. Upon excitation of these mixture systems in aqueous medium at 340-380 nm, fluorescence microscope photos were taken. The samples in aqueous medium were prepared by taking a drop of mixture solution on a glass slide and covered with a cover slip, and the fluorescence microscope photos were collected quickly. The samples at dry state were prepared by taking a drop of mixture solution on a glass slide and dried at room temperature.

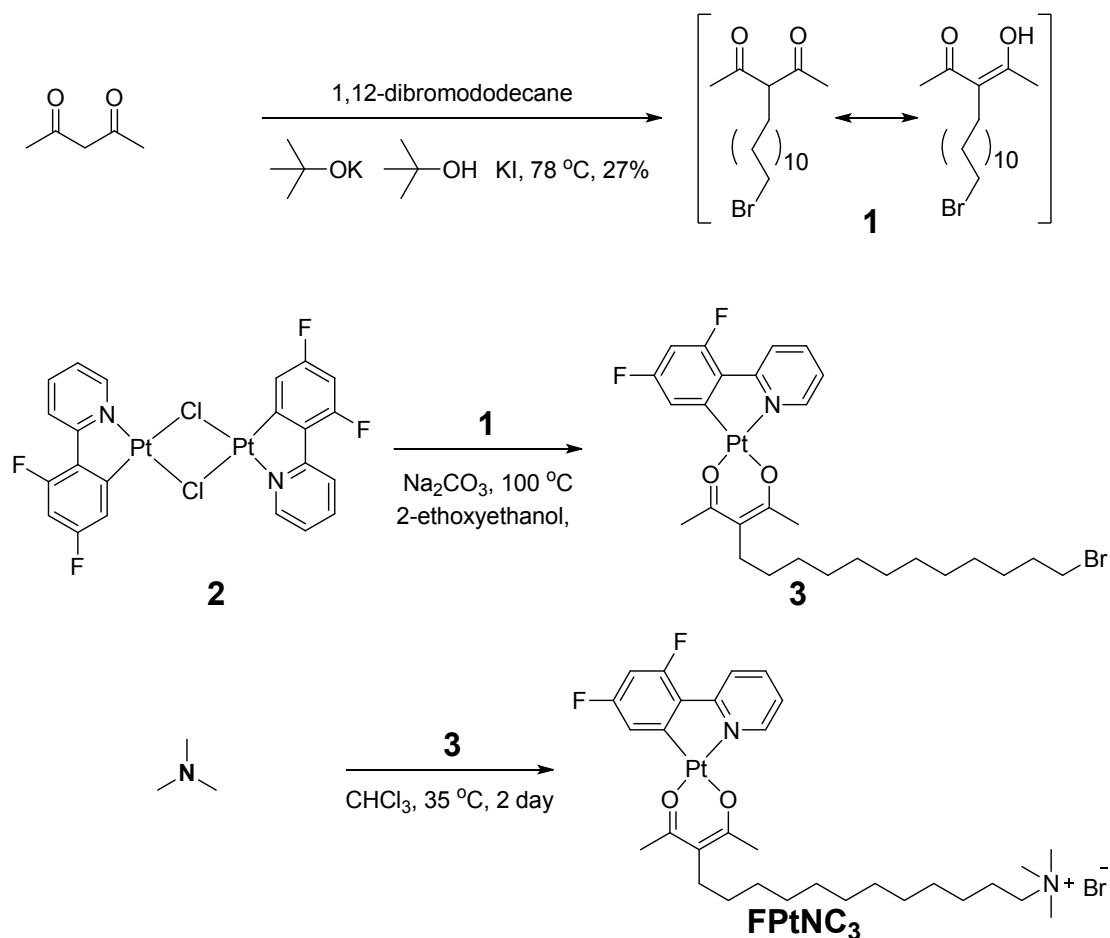
SEM Experiments

A drop of aqueous solution of mixture was placed on a glass slide and dried at room temperature. A conductive cover was coated before the SEM images were collected.

TEM Experiments

Bright-field TEM images were obtained with a FEI Tecnai F30 operating at 300 kV. A drop of aqueous solution of mixture was placed on a carbon coated copper grid, and dried at room temperature.

2. Synthetic route of FPtNC₃ complex



Scheme 1 Synthetic route of FPtNC₃ complex

1) Synthesis of 1. A mixture of 1, 12-Dibromododecane (9.84 g, 0.03 mol, 1 eq), Potassium tert-butoxide (3.37 g, 0.03 mol, 1 eq), KI (0.5 g, 0.003 mol, 0.1 eq), were dissolved in tert-Butanol (150 mL) under N₂. After stirring the solution at room temperature for 5 min, acetylacetone (3.0 g, 0.03 mol, 1 eq) was added slowly over a period of 2 min. Then the reaction mixture was heated to 75°C for 48 h, where complete reaction was observed by thin layer chromatography. After cooling, water was added and washed with CH₂Cl₂ and dried over anhydrous MgSO₄, filtered and concentrated. The product was purified using silica gel chromatography (petroleum ether/EtOAc, v/v, 100/1) to give a colourless viscous liquid (27.0 % yield).

¹H NMR (400 MHz, CDCl₃, Me₄Si): δ 16.70 (s, 0.4H, COH enol-form), 3.61 (t, 0.5H, COCHCO, keto-form), 3.41 (t, 2H, J = 7 Hz, CH₂Br), 2.20-2.23 (m, 1.1H, enol form CH₂(CH₂)₁₁Br), 2.17 (s, 3H, CH₃COCHCOCH₃, keto-form), 2.13 (s, 3H, CH₃COCHCOCH₃, enol-form), 1.80-1.89 (m, 1.3H, CHCH₂(CH₂)₁₁Br, keto-form; 2H, e, CH₂CH₂Br), 1.26-1.42 (m, 18H, BrCH₂CH₂(CH₂)₈).

¹³C NMR (100 MHz, CDCl₃, Me₄Si): δ 204.43, 190.82, 110.49, 68.90, 33.95, 32.71, 30.58, 29.50, 29.45, 29.40, 29.31, 29.17, 28.97, 28.64, 28.22, 28.05, 27.49, 27.44, 22.76.

HR-ESI-MS m/z : calcd [C₁₇H₃₂BrO₂]⁺ : 347.1580; found [C₁₇H₃₂BrO₂]⁺ : 347.1583.

2) Synthesis of 2. **2** was synthesized by the literature methods.^[1]

3) Synthesis of 3. A mixture of **1** (2.5 g, 7.2 mmol, 2.5 eq), **2** (2.4 g, 2.85 mmol, 1 eq), and

Na₂CO₃ (3.0 g, 28.3 mmol, 10 eq) in 2-ethoxyethanol (50 mL), was sealed under N₂ and heated to 100°C for 16 h. The cooled mixture was diluted in CH₂Cl₂ and filtered, the solvent was removed under reduced pressure, and the compound was purified by flash chromatography (petroleum ether/dichloromethane, v/v, 10/1). The product was recrystallized with dichloromethane/methanol (20.0% yield).

¹H NMR (400 MHz, CDCl₃, Me₄Si): δ 1.25-1.43 (m, 18H, BrCH₂CH₂(CH₂)₈), 1.82-1.87 (m, 2H, CH₂CH₂Br), 2.14, 2.16 (2s, 6H, CH₃COCHCOCH₃), 2.32 (t, J = 8 Hz, 2H, CH₂(CH₂)₁₁Br), 3.42 and 3.54 (2 × t, J = 8 Hz, 2H, CH₂Br), 6.53-6.60 (m, 1H), 7.09-7.14 (m, 2H), 7.82 (t, J = 8 Hz, 1H), 7.95 (d, J = 8 Hz, 1H), 8.97 (d, J = 8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, Me₄Si): δ 184.73, 182.58, 165.15 (d, J = 8 Hz), 161.27, 158.52 (d, J = 13 Hz), 146.98, 144.66, 144.62 (d, J = 8 Hz), 138.42, 128.10 (q, J = 2 Hz), 122.17 (d, J = 18 Hz), 120.91, 112.13, 99.00 (t, J = 27 Hz), 45.21, 34.10, 32.81, 32.63, 30.97, 30.91, 29.90, 29.67, 29.58, 29.52, 29.45, 29.41, 28.87, 28.75, 28.16, 27.58, 26.87, 26.77.

HR-ESI-MS m/z : calcd [C₂₈H₃₆BrF₂NO₂PtNa]⁺ : 754.1402; found [C₂₈H₃₆BrF₂NO₂PtNa]⁺ : 754.1437.

4) Synthesis of FPtNC₃. Under a nitrogen atmosphere complex **3** (0.26 g, 0.36 mmol, 1 eq) was dissolved in CHCl₃ (7 mL) followed by the addition of trimethylammonium (3.1 g, 17.3 mmol, 46 eq), the reaction mixture was stirred at 35°C for three days. After cooling, the CHCl₃ was removed under reduced pressure, the compound was purified by flash chromatography (petroleum ether/dichloromethane, v/v, 20/1), then was recrystallized by diffusing diethyl ether to **4** in CH₂Cl₂/CH₃OH to get yellow solid (40% yield).

¹H NMR (400 MHz, CDCl₃, Me₄Si): δ 1.25-1.41 (m, 18H, CH₂(CH₂)₉CH₂CH₂N⁺), 1.71 (m, 2H, CH₂CH₂N⁺(CH₃)₃), 2.14 and 2.16 (2s, 6H, CH₃COCHCOCH₃), 2.32 (t, J = 8 Hz, 2H, CH₂(CH₂)₁₁N⁺(CH₃)₃), 3.42 (s, 9H, CH₂N⁺(CH₃)₃), 3.54-3.58 (m, 2H, CH₂N⁺), 6.53-6.59 (m, 1H), 7.07-7.12 (m, 2H), 7.82 (t, J = 8 Hz, 1H), 7.95 (d, J = 8 Hz, 1H), 8.97(d, J = 8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, Me₄Si): δ 184.58 (s), 182.16 (s), 164.74 (d, J = 6 Hz), 160.95, 160.83, 158.38, 146.74, 144.73, 144.65, 138.27, 128.10 (q, J = 2 Hz), 121.83 (d, J = 7 Hz), 120.85, 111.94, 98.70 (t, J = 27 Hz), 66.63, 53.15, 30.81, 30.73, 29.71, 29.45, 29.34, 29.24, 29.18, 29.04, 27.41, 26.63, 25.94, 23.01.

HR-ESI-MS m/z : calcd [C₃₁H₄₅F₂N₂O₂Pt]⁺: 710.3094; found [C₃₁H₄₅F₂N₂O₂Pt]⁺: 710.3093.

3. Spectrum Analysis

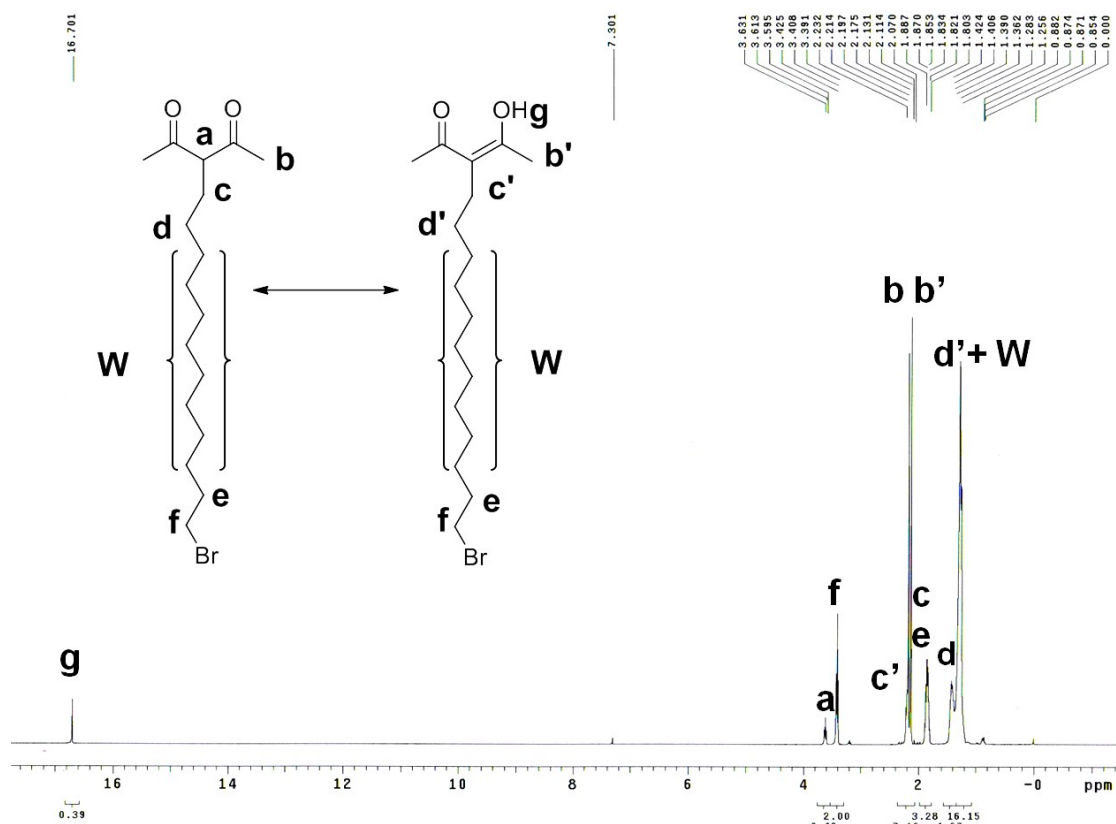


Figure S1 The ^1H NMR of complex 1

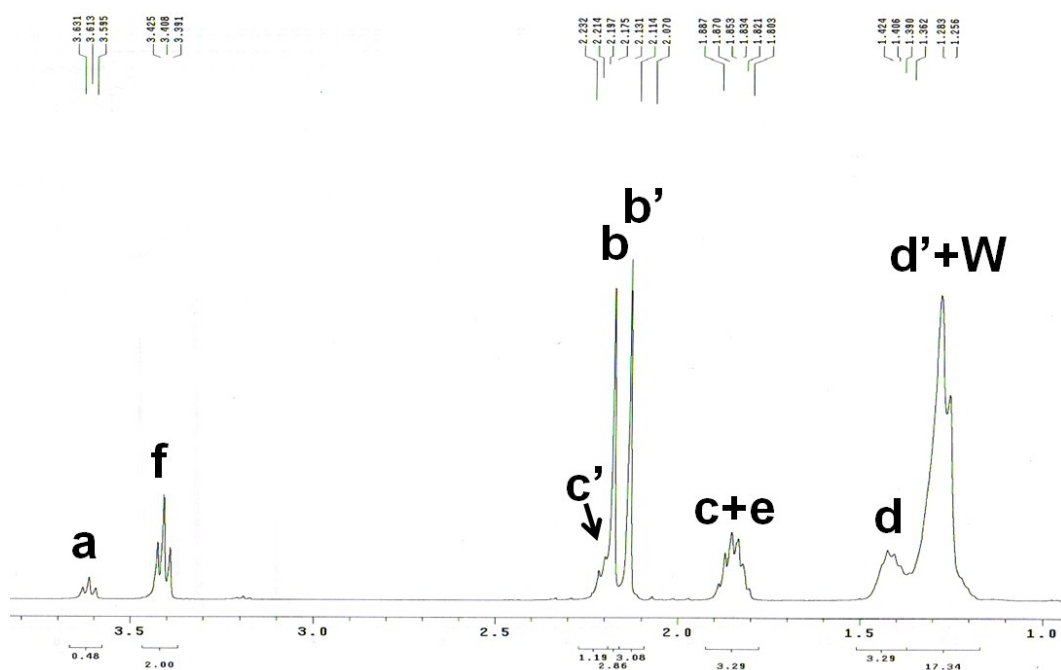


Figure S2 A part of ^1H NMR of complex 1

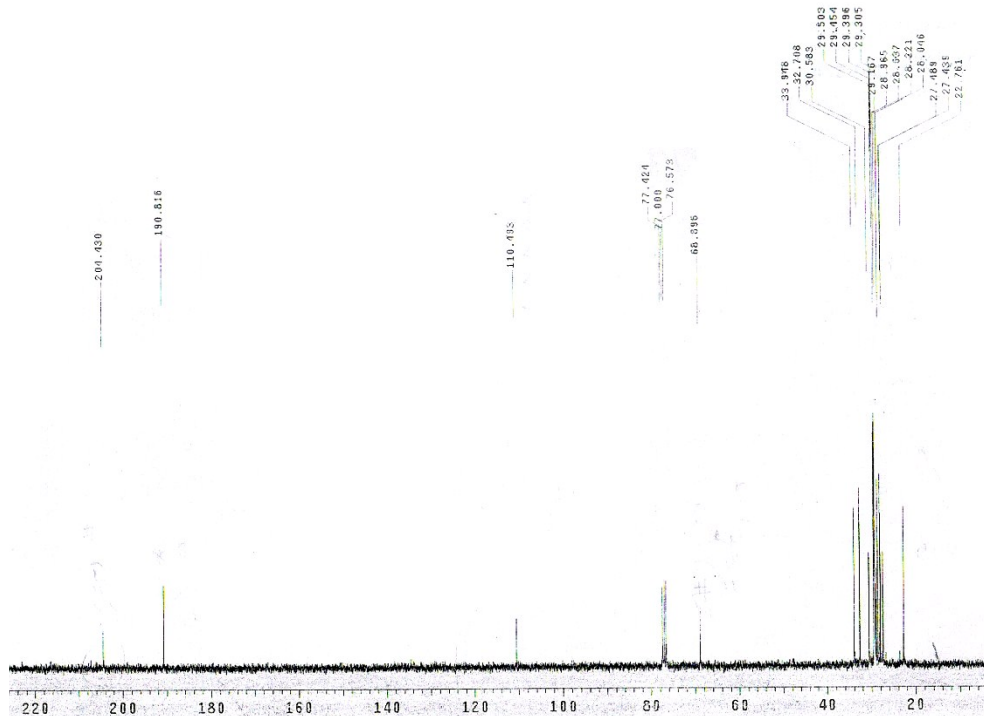


Figure S3 The ^{13}C NMR of complex 1

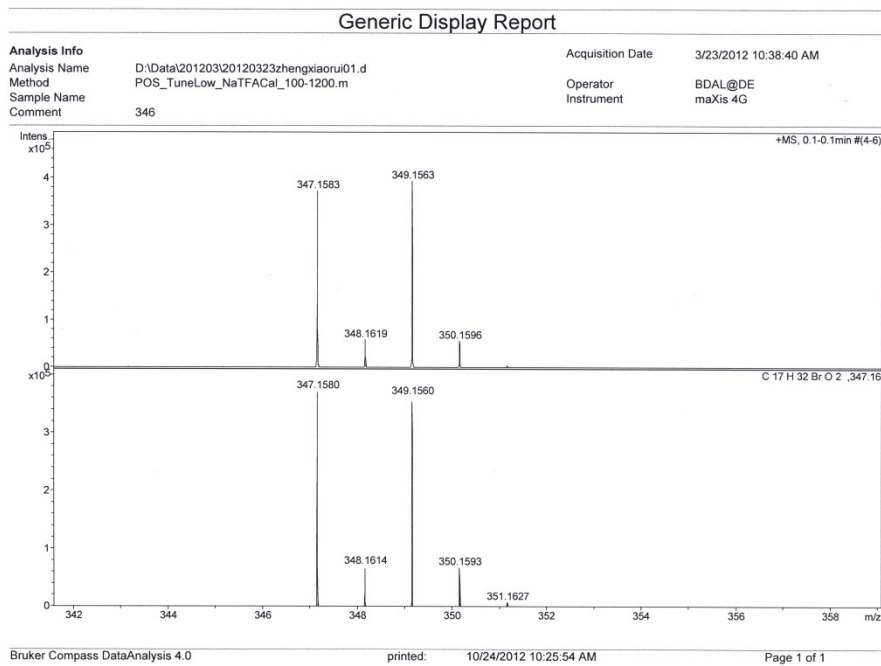


Figure S4 The HR-ESI-MS of complex 1

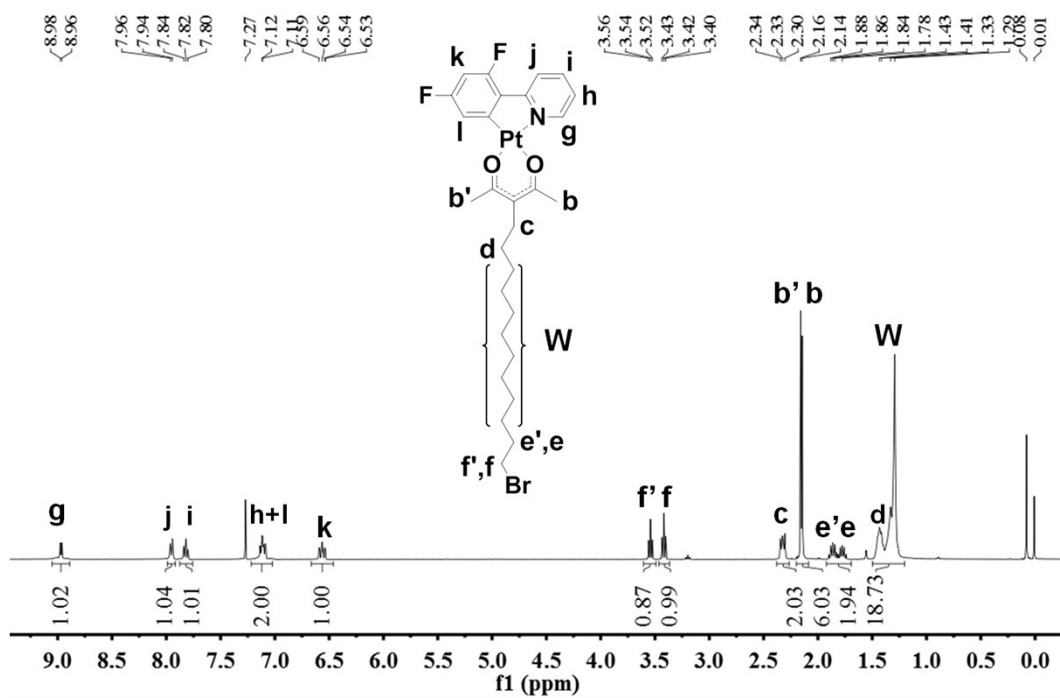


Figure S5 The ¹H NMR of complex 3

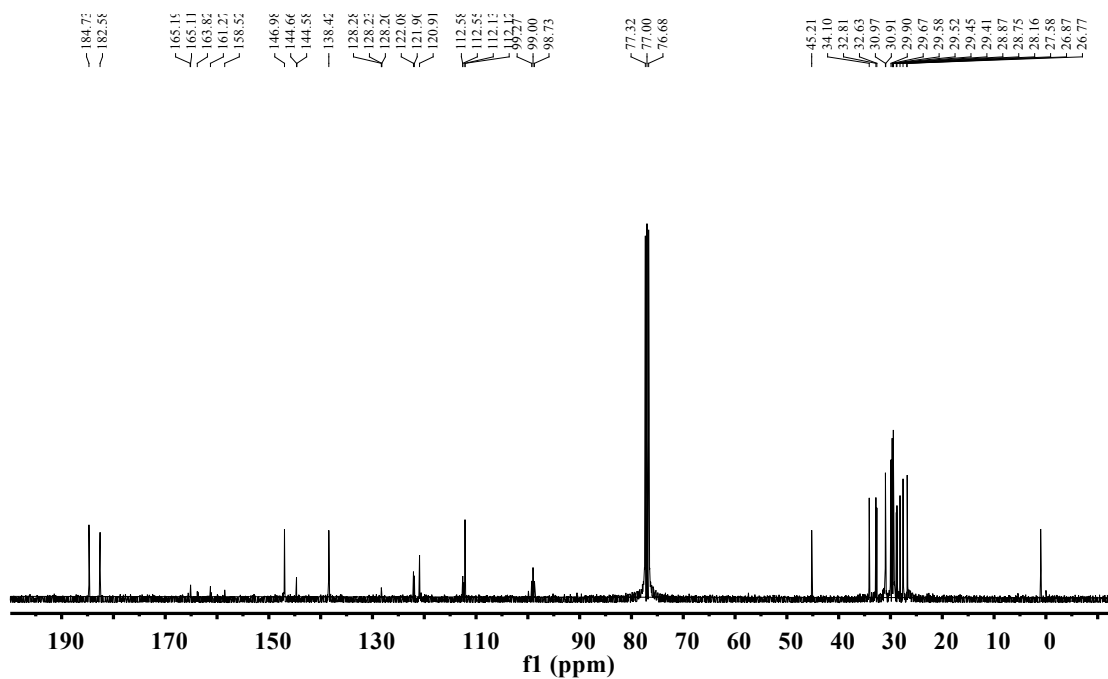
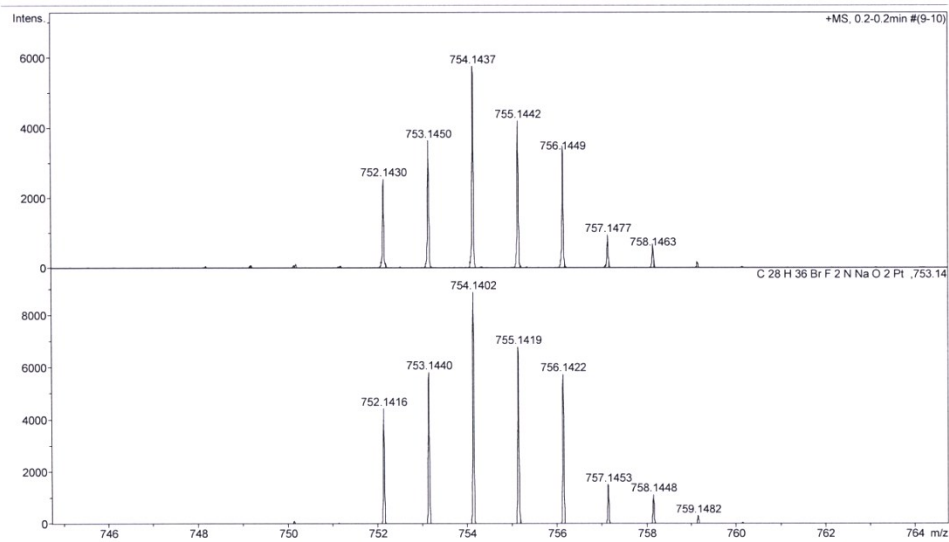


Figure S6 The ¹³C NMR of complex 3

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Sample Name		Operator
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		maXis 4G



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Figure S7 The HR-ESI-MS of complex **3**

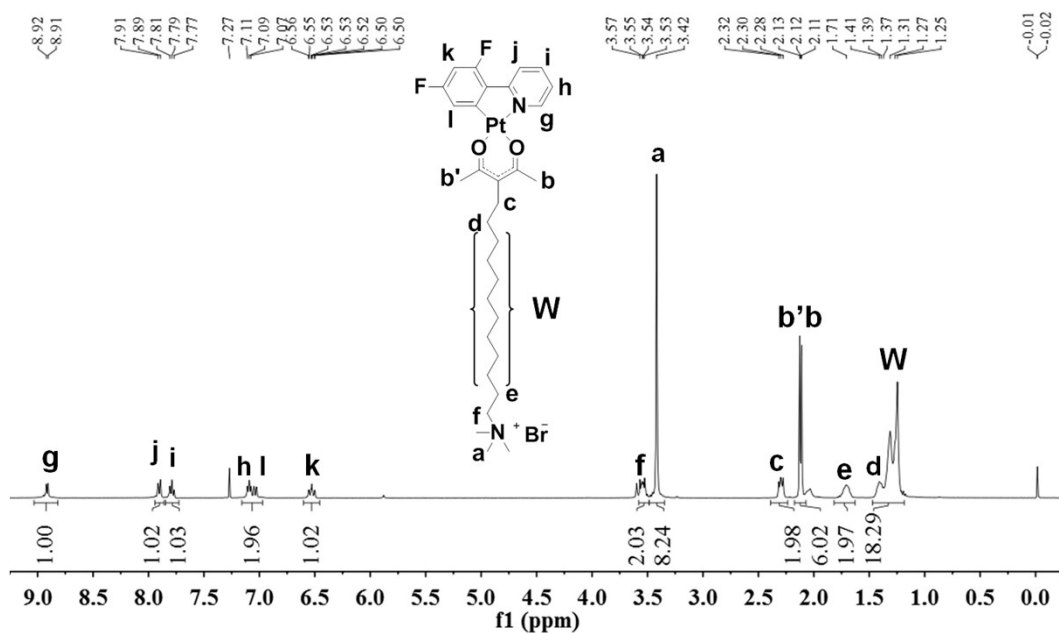


Figure S8 The ¹H NMR of FPtNC₃

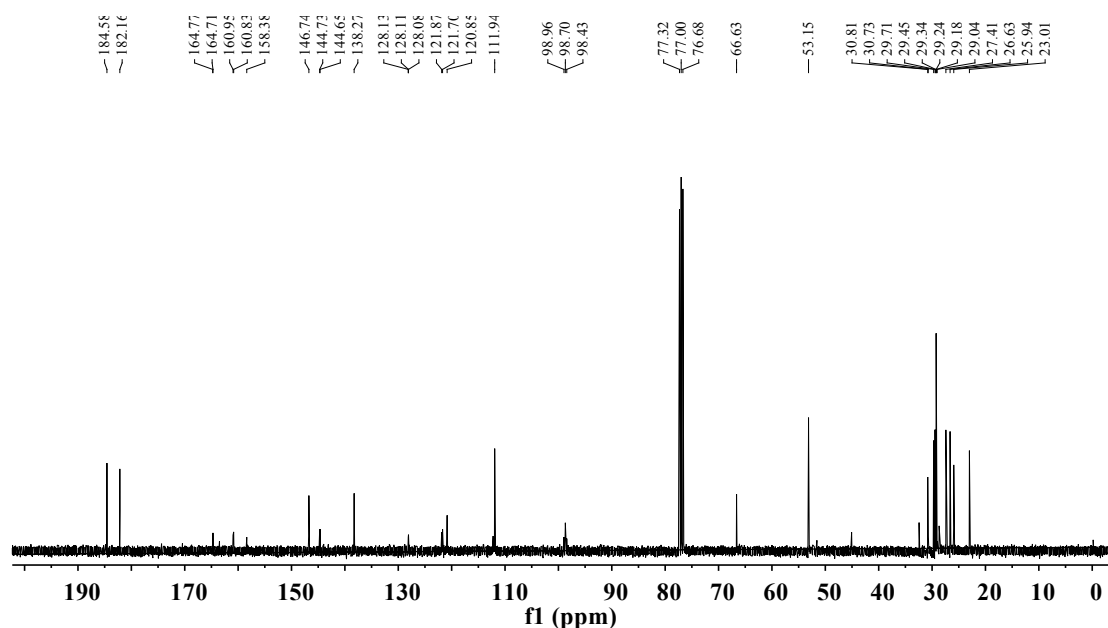


Figure S9 The ^{13}C NMR of FPtNC₃

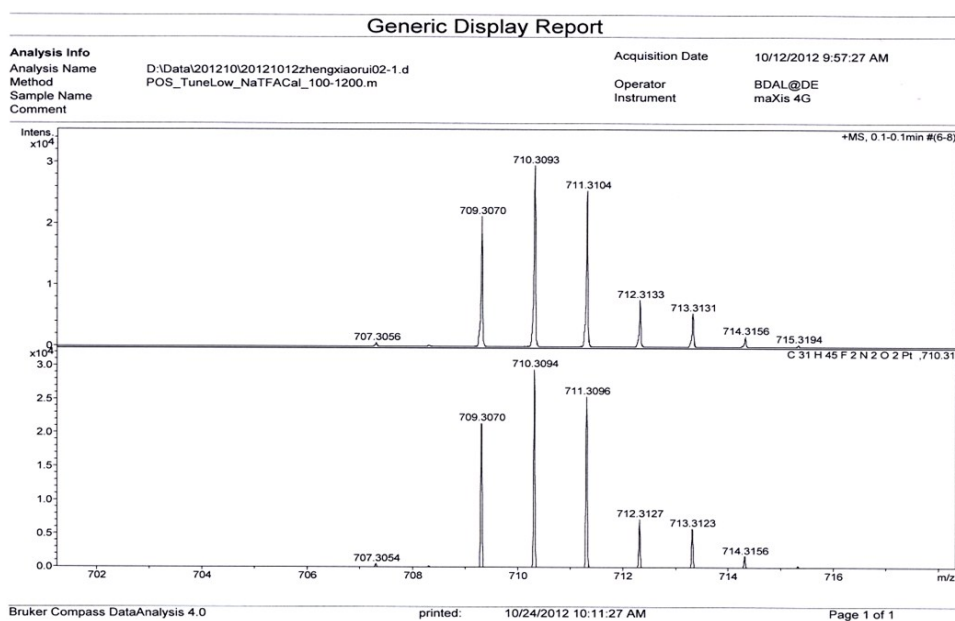


Figure S10 The HR-ESI-MS of FPtNC₃

3. Self-assembly of FPtNC₃ and FPtNC₃/DTAB mixtures in water

Solution Preparation

The concentration of FPtNC₃ aqueous solution was maintained at 0.2 mM. The samples of assemble systems were prepared by adding the DTAB aqueous solution to FPtNC₃ solution and aging for several months to get suspension solutions. Longer aging do not result in change in samples. Assemble and some measurements were repeated to ensure the reproducibility.

Table 1 The molar ratio of FPtNC₃/DTAB mixture systems and concentrations in detail.

The molar ratio of FPtNC ₃ /DTAB	The volume of FPtNC ₃ (0.2 mM) / mL	The volume of DTAB		Total concentration / mM	Total wt%	The percent of FPtNC ₃
		(0.02 M) / μ L	(0.2 M) / μ L			
1 : 0	4	0	0	0.20	13.6	100%
1 : 1	4	40	0	0.40	18.0	50%
1 : 2	4	80	0	0.59	21.8	33.3%
1 : 3	4	0	12	0.80	25.5	25%
1 : 4	4	0	16	0.99	28.8	20%
1 : 5	4	0	20	1.19	31.6	16.7%
1 : 6	4	0	24	1.39	34.4	14.3%
1 : 7	4	0	28	1.59	37.0	12.5%
1 : 8	4	0	32	1.79	39.2	11.1%
1 : 9	4	0	36	1.98	41.4	10.0%
1 : 10	4	0	40	2.18	43.3	9.09%
1 : 20	4	0	80	4.11	57.7	4.76%
1 : 30	4	0	120	5.96	66.1	3.23%
1 : 40	4	0	160	7.88	71.6	2.44%
1 : 50	4	0	200	9.71	75.5	1.96%
1 : 60	4	0	240	11.5	78.4	1.64%
1 : 70	4	0	280	13.3	80.7	1.41%
1 : 80	4	0	320	15.0	82.3	1.23%
1 : 90	4	0	360	16.7	84.0	1.10%
1 : 100	4	0	400	18.4	85.2	0.99%

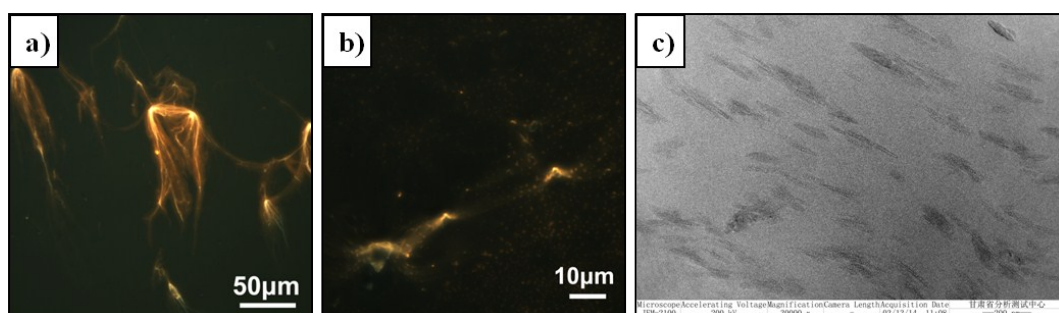


Figure S11 Fluorescent micrograph of FPtNC₃ in aqueous solution(a) and in dry state(b), (c)TEM image of FPtNC₃ in dry state on carbon casted copper grid.

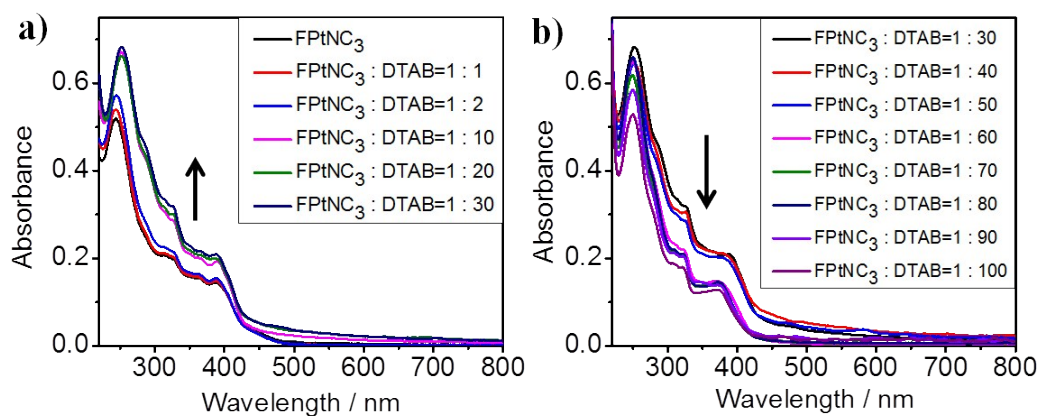


Figure S12 UV-Vis spectrum of FPtNC₃/DTAB mixture systems.

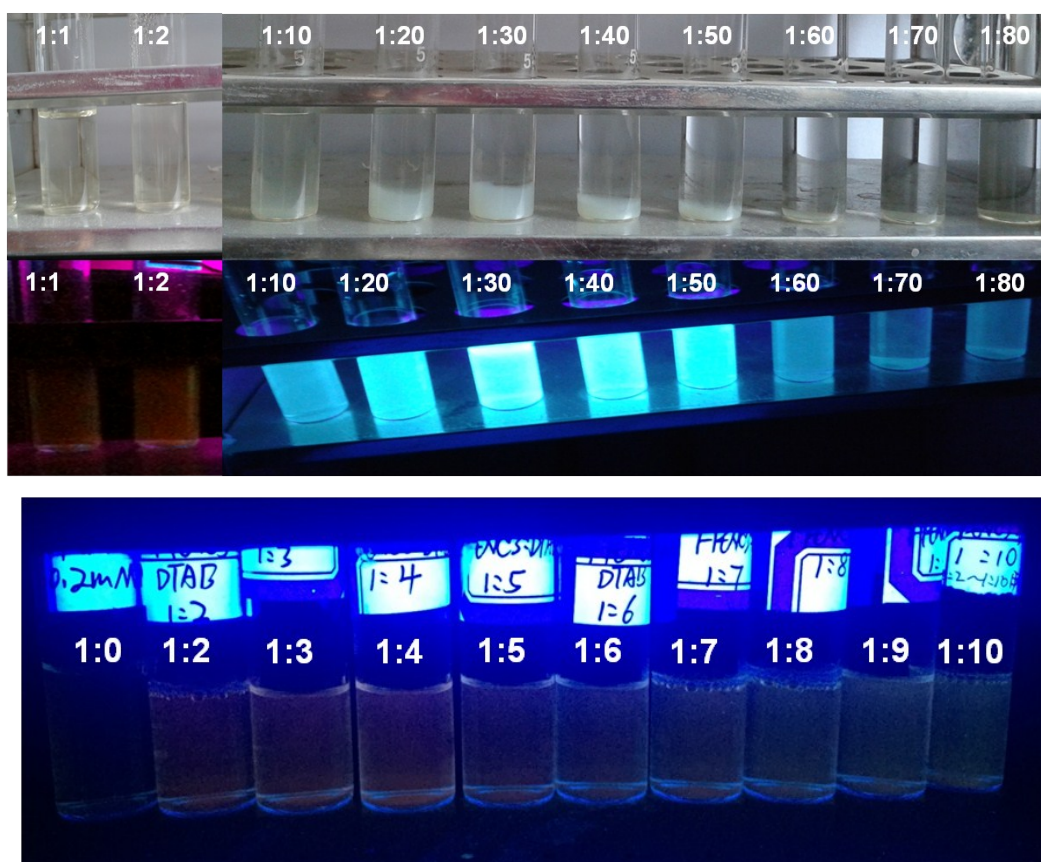


Figure S13 Photographic images of mixture systems excited at 365 nm wave length with a UV lamp.

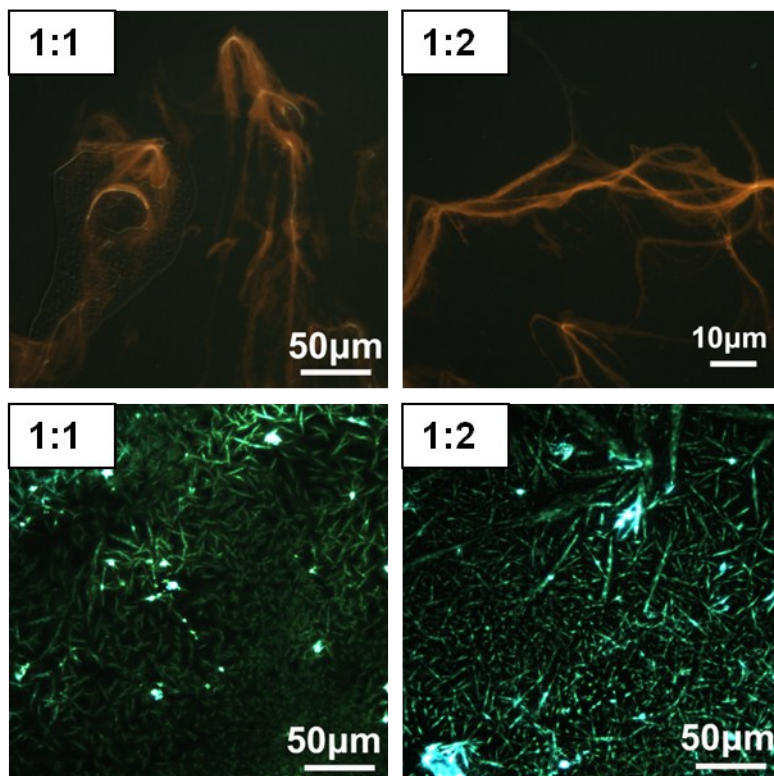


Figure S14 Fluorescent micrograph of FPtNC₃/DTAB mixture systems with molar ratio at 1:1 and 1:2 in aqueous solution(up) and in dry state(down).

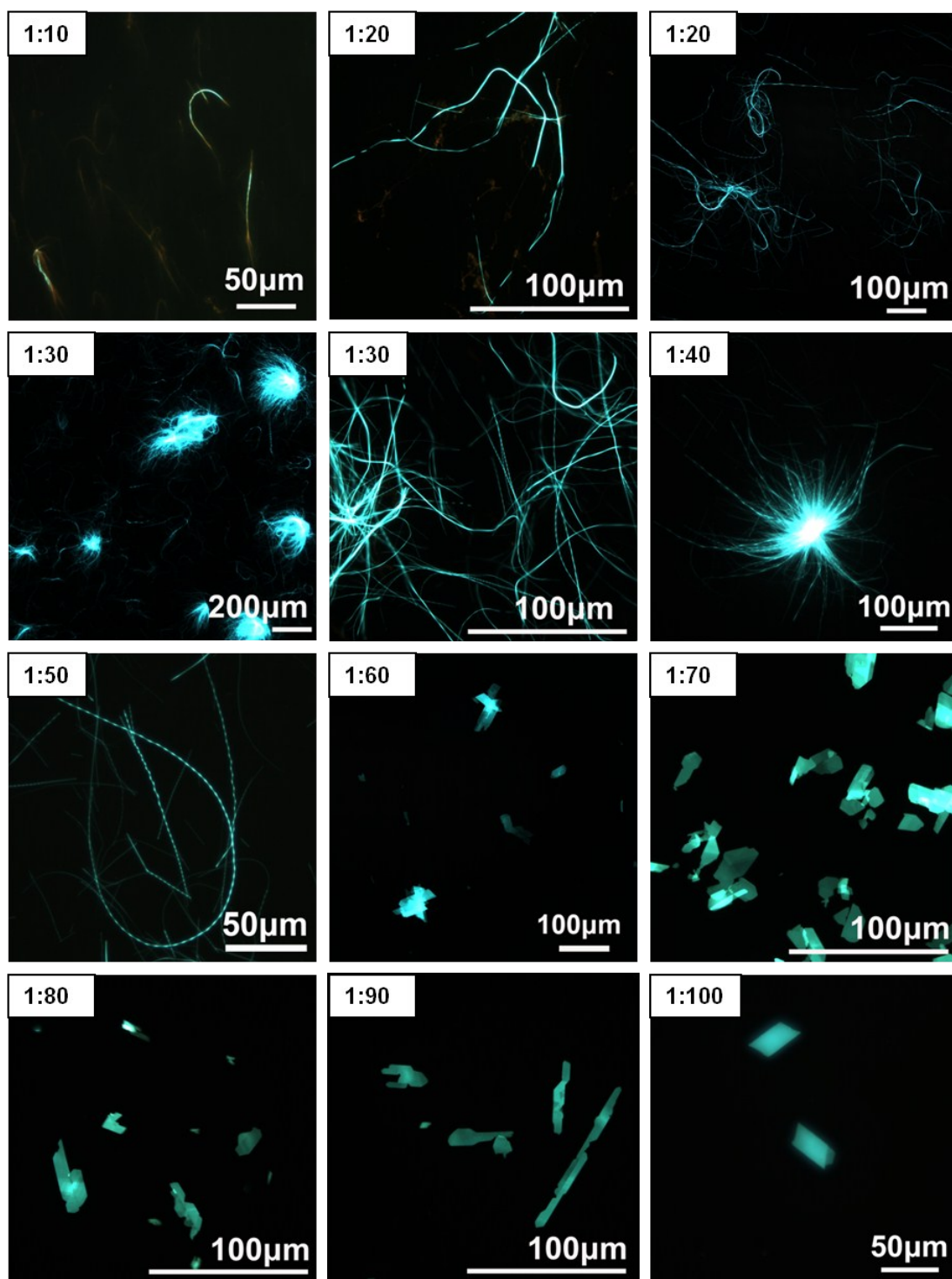


Figure S15 Fluorescent micrograph of FPtNC₃/DTAB mixture systems in aqueous medium.

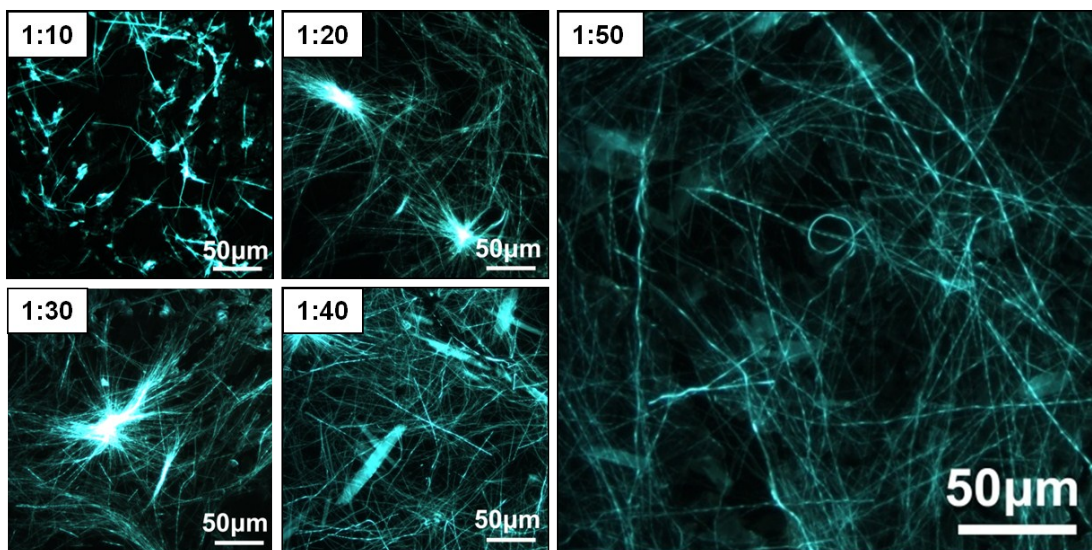


Figure S16 Fluorescent micrograph of FPTnC₃/DTAB mixture systems in dry state.

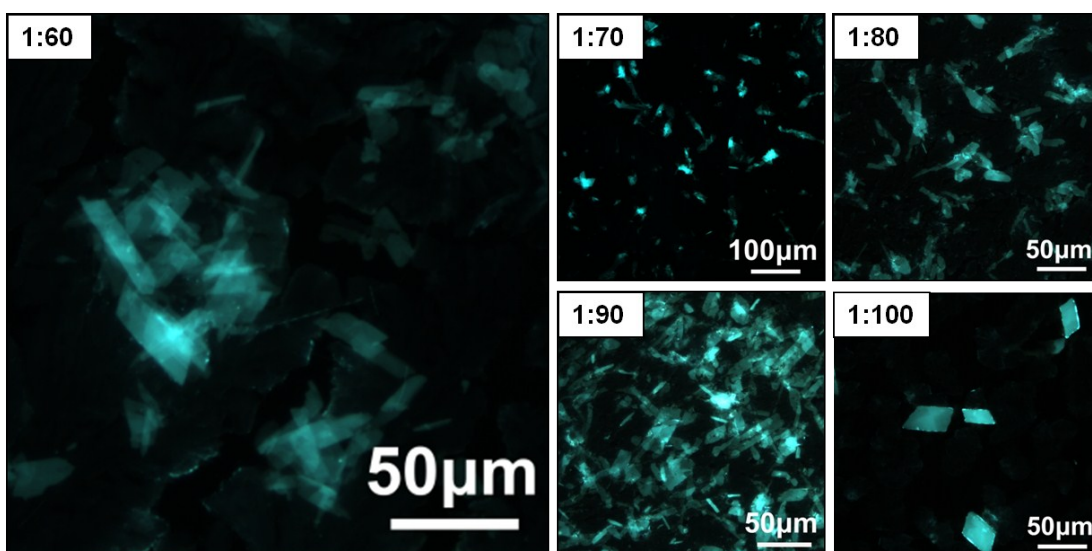


Figure S17 Fluorescent micrograph of FPTnC₃/DTAB mixture systems in dry state.

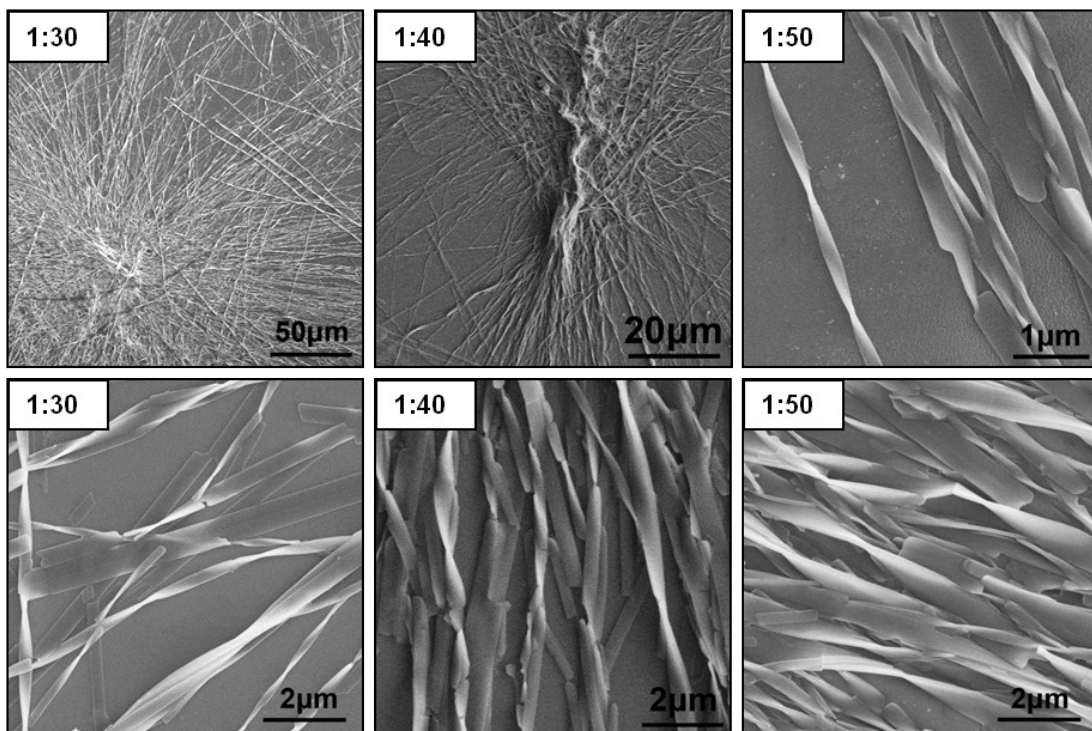


Figure S18 SEM images of FPtNC₃/DTAB mixture systems.

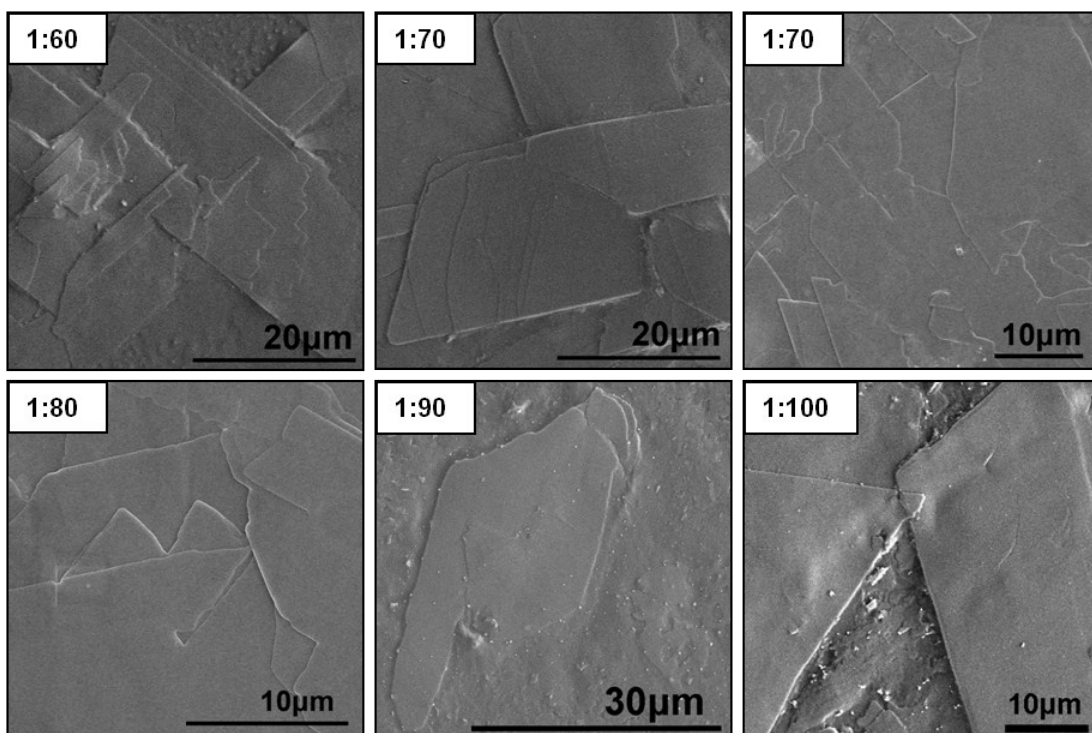


Figure 19 SEM images of FPtNC₃/DTAB mixture system.

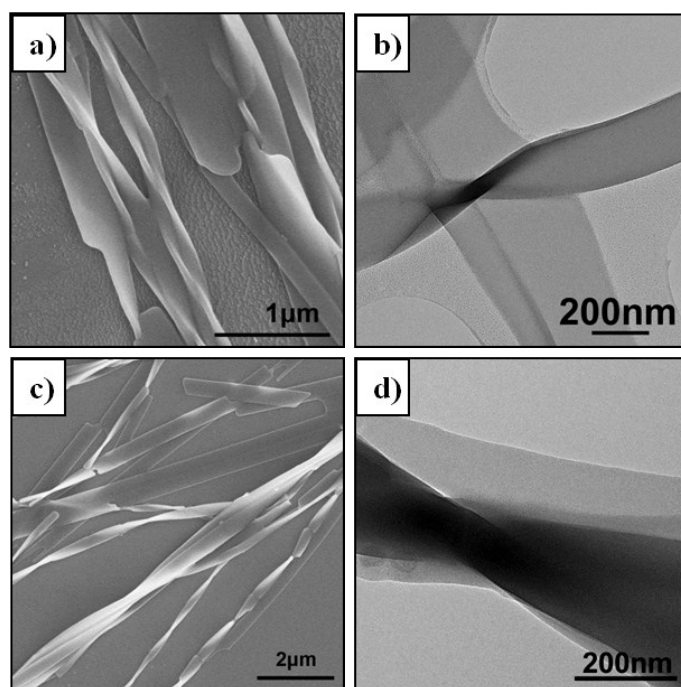


Figure S20 SEM images of FPtNC₃/DTAB mixture system with left hand(a, b), right hand(c, d) helices and a few straight ribbons.

References:

- 1 J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2002, **41**, 3055.