

Electronic Supplementary Information

Aqueous Solubilization of Hydrophobic Tetrapyrrole Macrocycles by Attachment to an Amphiphilic Single-Chain Nanoparticle (SCNP)

Rui Liu,^a Sijia Liu,^a Gongfang Hu, and Jonathan S. Lindsey*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

^aEqual contributions by both authors.

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1. Characterization of Amphiphilic Polymer F-Ph

The ¹H NMR spectrum of the second batch of **F-Ph** in D₂O (Figure S1) exhibits chemical shifts identical with those of the previous batch of **F-Ph**.³⁰ Three pendant units are labeled in distinct color: **PEGA** (green), **LA** (blue) and **AMPS** (red). The integrals of the terminal methyl of **PEGA**, the terminal methyl of **LA** and the gem-dimethyl of **AMPS** indicate the 1:1:5 ratio of pendant groups, as expected on the basis of the 1:1:5 ratio of initial reactants.

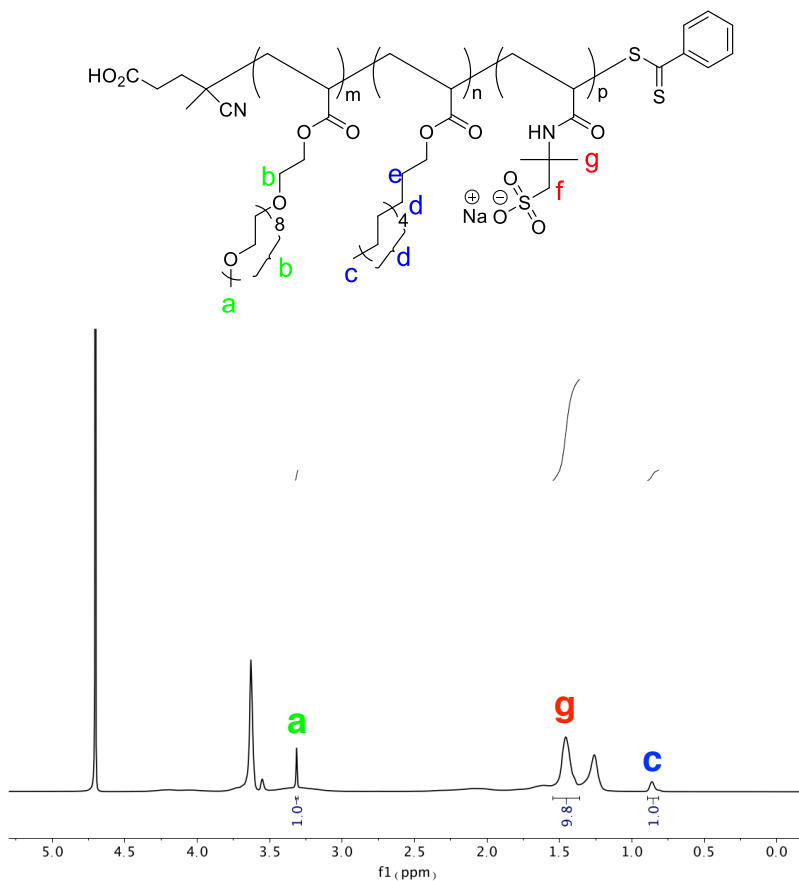


Figure S1. ^1H NMR spectra of **F-Ph** in D_2O at room temperature.

The ^1H NMR spectra of the second batch of **F-Ph** were also collected in 0.25 M NaCl D_2O solution, CD_3OD , and $\text{DMSO-}d_6$ (Figure S2). The peak of **LA** (d) in $\text{DMSO-}d_6$ is sharper (higher) than that in CD_3OD and 0.25 M NaCl D_2O solution, which indicates a more dispersed distribution of hydrophobic pendant groups in $\text{DMSO-}d_6$. In contrast, the gem-dimethyl peak (g) of **AMPS** in 0.25 M NaCl D_2O solution is sharper (higher) than that in CD_3OD and $\text{DMSO-}d_6$. The different shape of ^1H NMR in 0.25 M NaCl D_2O solution, CD_3OD , and $\text{DMSO-}d_6$ represent that **F-Ph** changed from folded form in 0.25 M NaCl D_2O solution to extended form in $\text{DMSO-}d_6$.

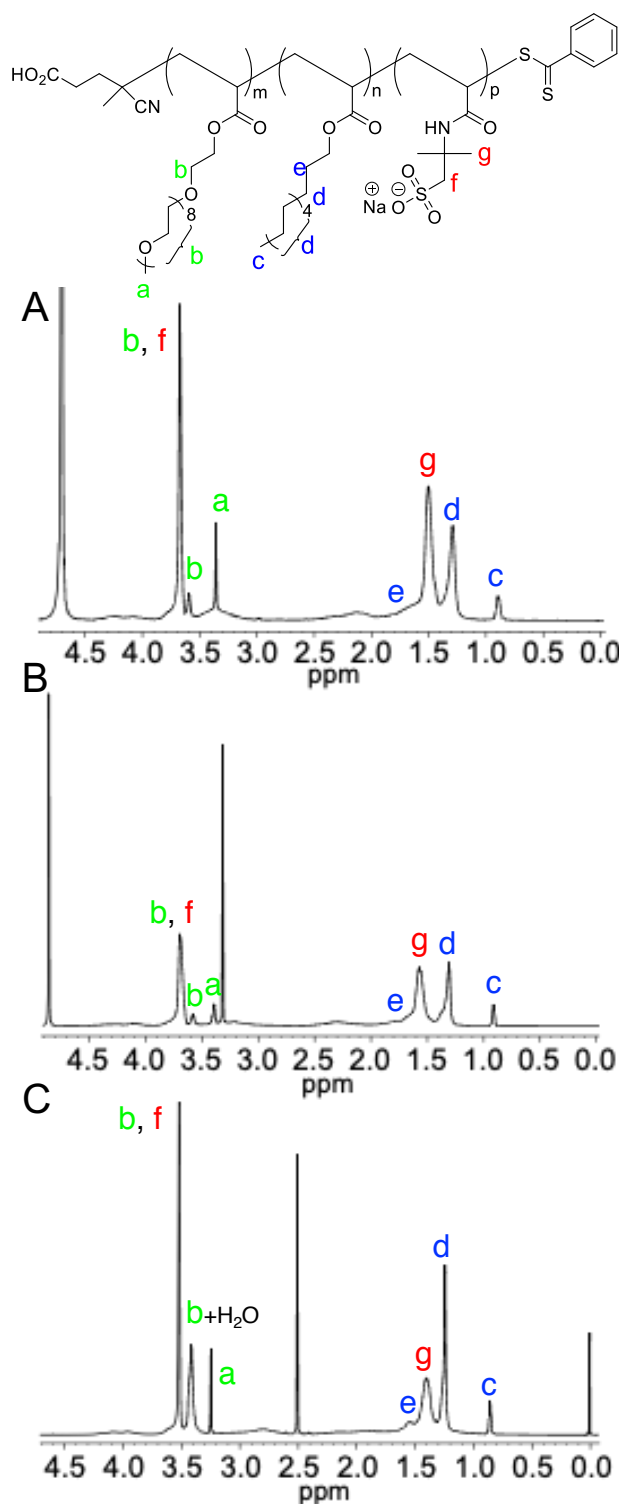


Figure S2. ^1H NMR spectra at room temperature of **F-Ph** in (A) 0.25 M NaCl D_2O solution; (B) CD_3OD ; and (C) $\text{DMSO-}d_6$.

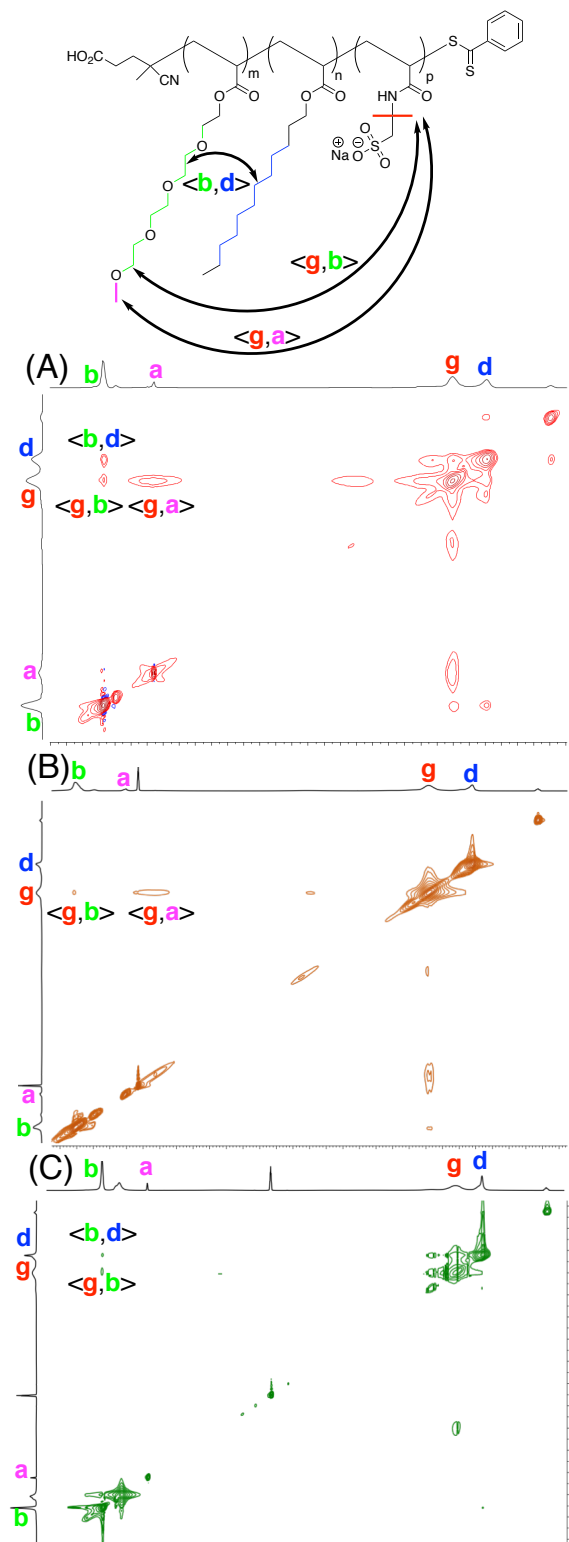


Figure S3. (A) Illustration of NOESY correlations of **F-Ph**; 2D NOESY data: NOESY spectrum of **F-Ph** in (B) 0.25 M NaCl aqueous solution; (C) CD₃OD; and (D) DMSO-*d*₆. All data were collected at room temperature.

To gain insights concerning possible morphology of the polymer, NOESY experiments were carried out in 0.25 M NaCl D₂O solution, CD₃OD, and DMSO-*d*₆, using the same polymer concentration in each (20 mg/mL). In 0.25 M NaCl D₂O solution (Figure S3A), the NOESY experiment shows strongly correlated signals between two hydrogen atoms on different pendant chains. The cross peaks <g,a> and <g,b> suggest that the **PEGA** pendant units interact with the **AMPS** pendant units. The cross peak <b,d> from the ethylene groups (b) of **PEGA** and the backbone protons (e) of **LA** reveals that the polyethylene glycols are close to lauryl groups. In contrast, NOESY spectra of **F-Ph** in CD₃OD and DMSO-*d*₆ (Figures S3B and S3C) exhibit few cross peaks between different pendant chains, and the interactions between different pendant chains in organic solvents are weaker than those in the 0.25 M NaCl D₂O solution. A possibility is that in organic solvents the pendant units are more extended so that the interactions between each unit are less likely. In summary, the NOESY spectra are consistent with a folded structure of **F-Ph** in aqueous salt solution but unfolded structure in organic solvent, although the NOESY data alone, in the absence of DLS data, are insufficient to draw conclusions concerning folded or unfolded morphologies.

The absorption spectrum of **F-Ph** (Figure S4A) shows a characteristic peak at 300 nm due to the dithiobenzoate, which confirms the end group is intact for fluorophore conjugation via thiol-maleimide chemistry. Analytical SEC study of **F-Ph** carried out in DMF (Figure S4B) gave a M_n value of 36 kDa and a polydispersity index (PDI, $D = M_w/M_n$) value of 1.55. The PDI is consistent with the previous result, whereas the M_n is slightly lower than that of the previous batch of **F-Ph** (40 kDa).³⁰ The polymerization is reproducible in affording a similar size and degree of polymerization. DLS spectroscopy of **F-Ph** was carried out in 1 M NaCl aqueous solution at room temperature. The polymer self-folds in 1 M NaCl aqueous solution to give a compact unimer with an average hydrodynamic diameter of 13 nm (Figure S4C).

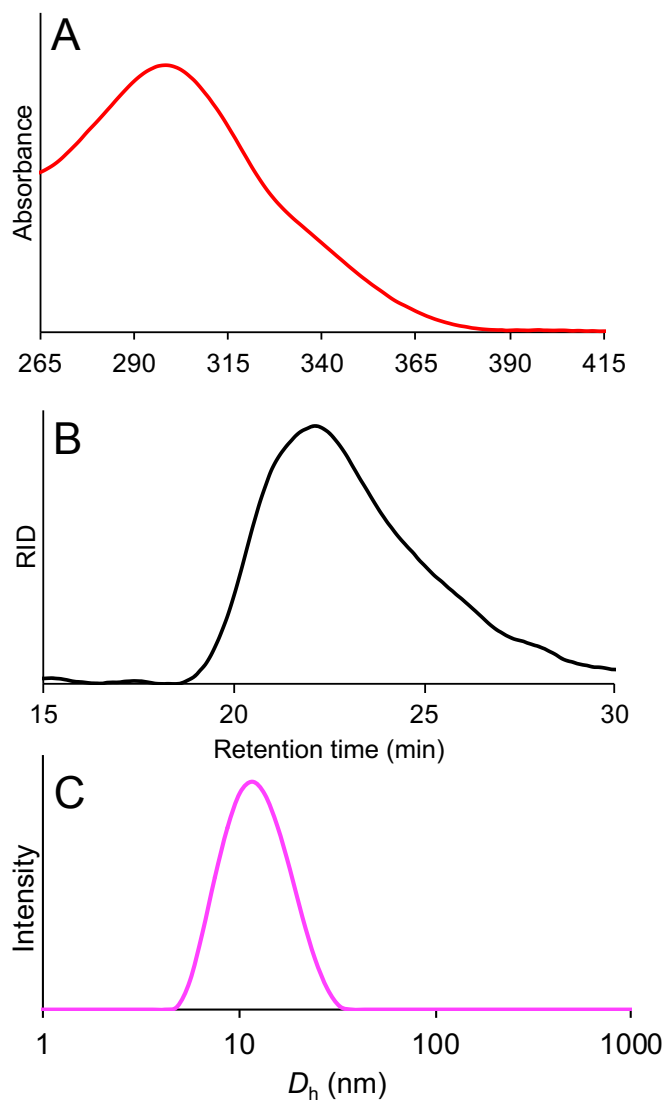


Figure S4. Data for the new batch of **F-Ph**. (A) Absorption spectrum in methanol; (B) analytical SEC trace in DMF; and (C) DLS in 1 M NaCl aqueous solution. All data were collected at room temperature.

2. Absorption and Fluorescence Spectral Properties

The unknown blue fluorescence of **Pod-ZnPc(*t*-Bu)₃** is shown in Figure S5.

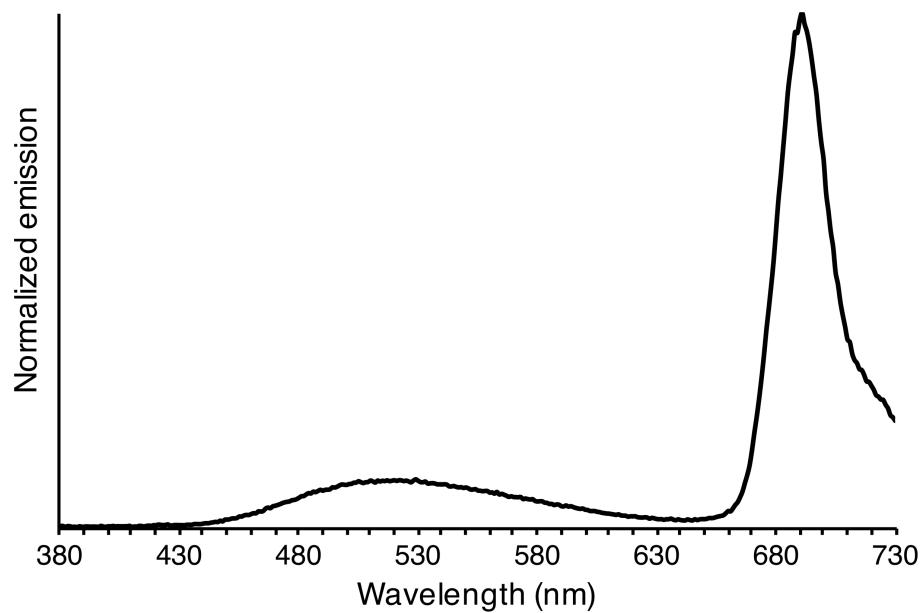


Figure S5. Fluorescence emission spectrum ($\lambda_{\text{ex}} = 370$ nm) of **Pod-ZnPc(*t*-Bu)₃** in 1 M NaCl aqueous solution at room temperature.

To understand the possible origin of the broadening of **Pod-PMI** in 1 M NaCl aqueous solution, the spectra of **PMI-mal** were collected in the mixture of cyclohexane (CH) and ethanol (Figure S5 and Table S1).

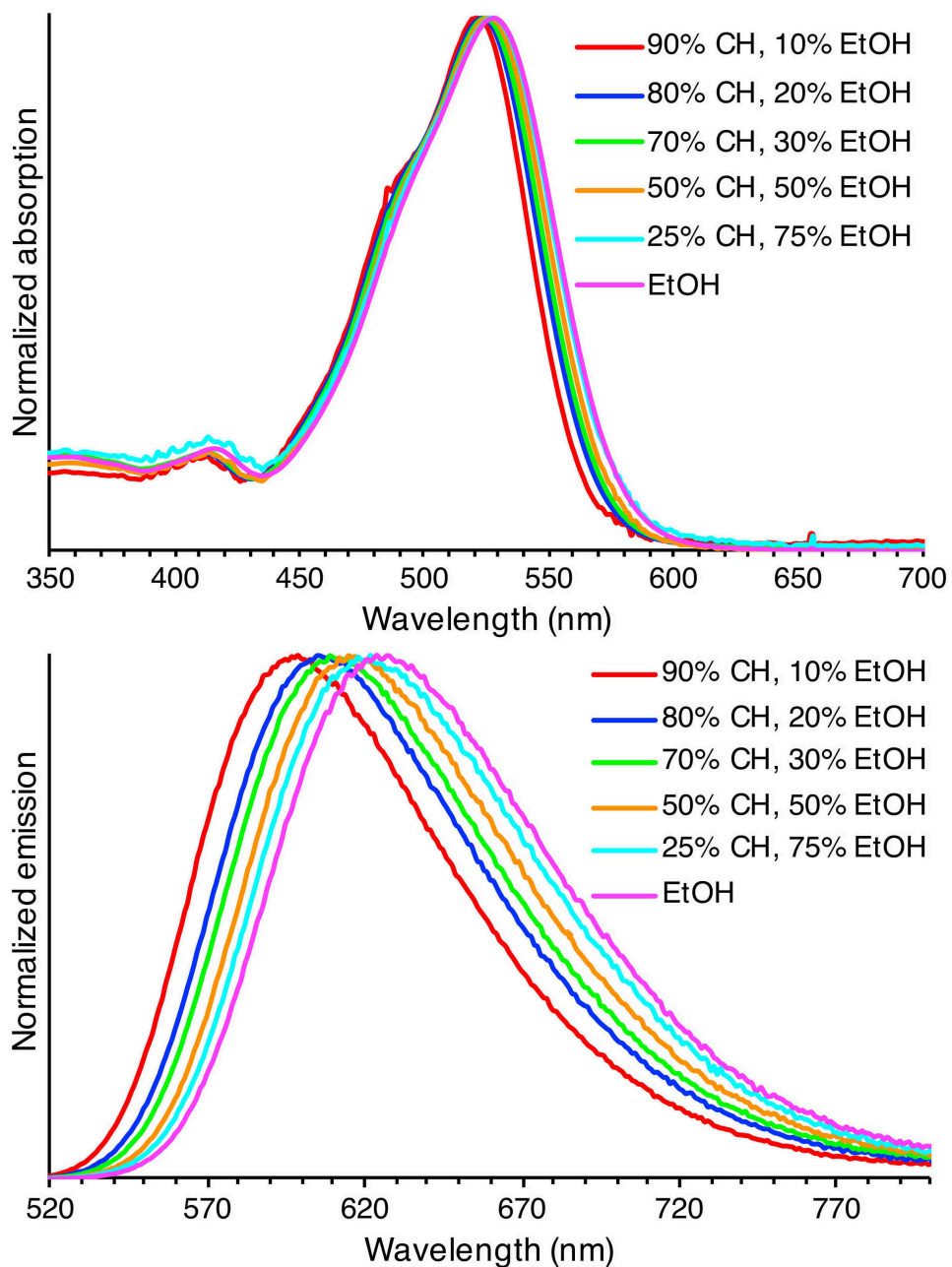


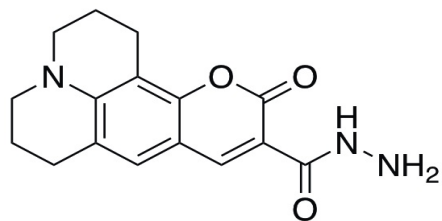
Figure S6. Absorption and emission of **PMI-mal** in the mixture of cyclohexane (CH) and ethanol. All data were collected at room temperature.

Table S1. Spectral properties of **PMI-mal** in various solvents.^a

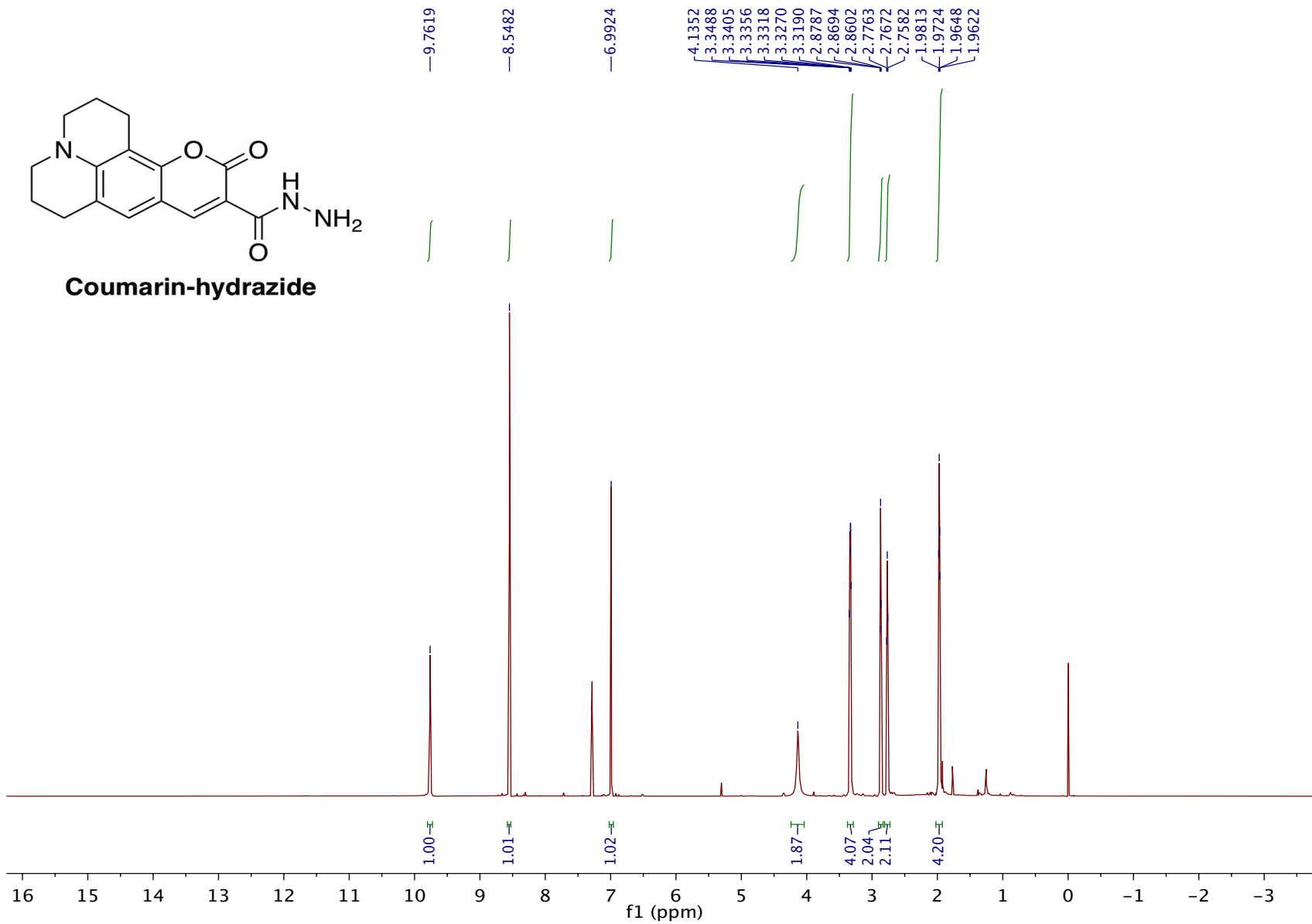
Solvent	λ_{abs} [fwhm] (nm)	λ_{exc} (nm)	λ_{em} [fwhm] (nm)	Φ_{f} ^b
toluene	529 [69]	413	574 [77]	0.66 ^b
90% CH, 10% EtOH	521 [74]	413	599 [97]	0.63 ^c
80% CH, 20% EtOH	523 [74]	413	605 [99]	0.54 ^c
70% CH, 30% EtOH	524 [75]	413	609 [100]	0.52 ^c
50% CH, 50% EtOH	526 [76]	413	615 [102]	0.49 ^c
75% CH, 25% EtOH	527 [78]	413	622 [105]	0.44 ^c
EtOH	528 [78]	413	624 [106]	0.41 ^c

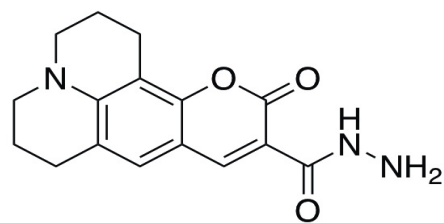
^aAll data were collected at room temperature. “CH” is cyclohexane. ^bReference 30. ^cUsing **PMI-mal** in toluene ($\Phi_{\text{f}} = 0.66$) as the standard.

3. NMR Spectral Data

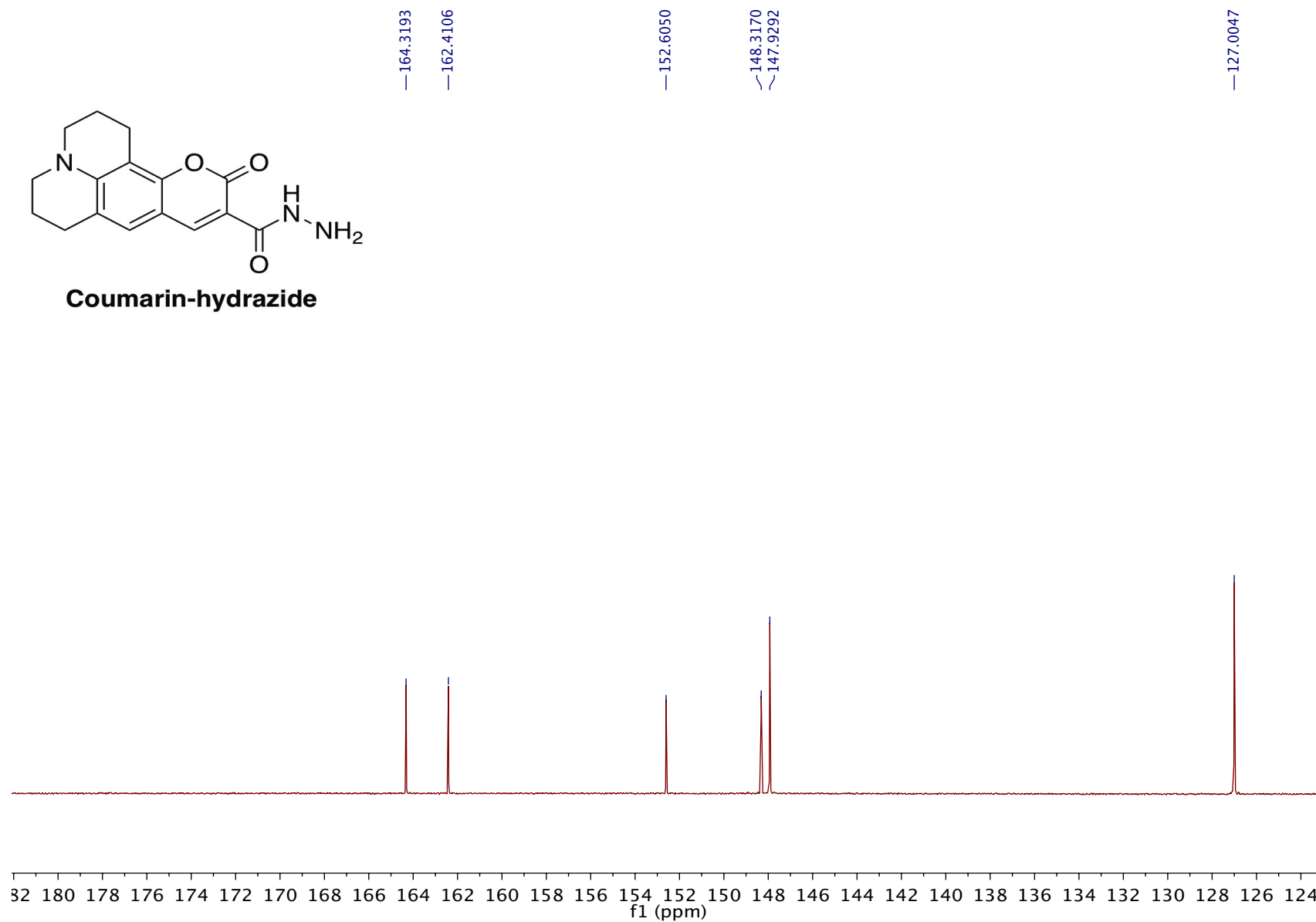


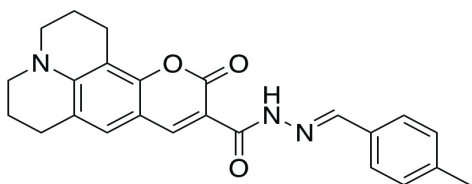
Coumarin-hydrazide



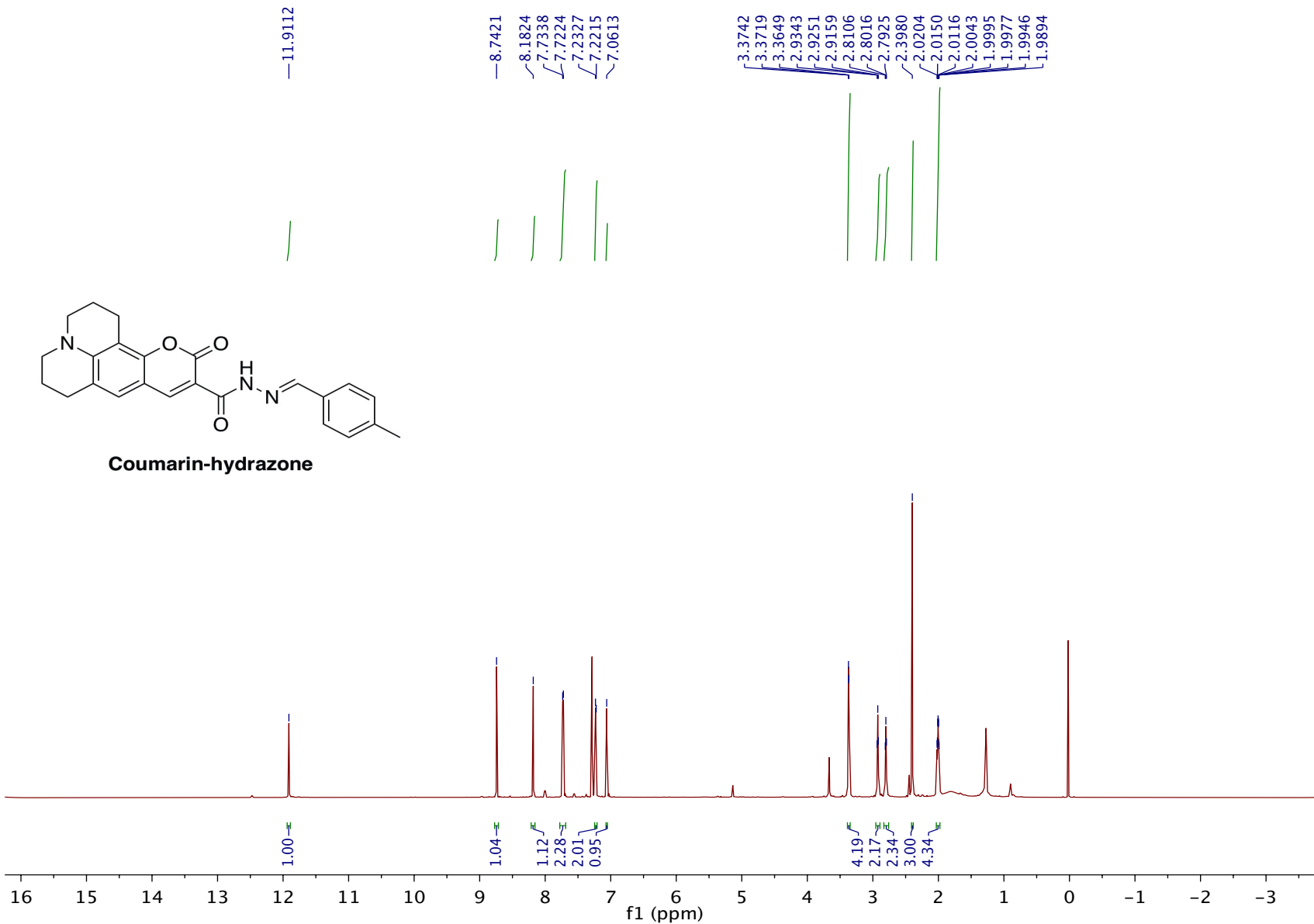


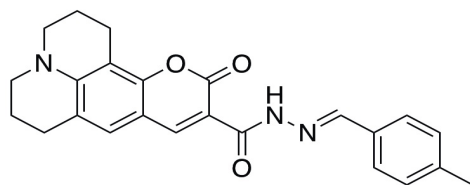
Coumarin-hydrazide





Coumarin-hydrazone





Coumarin-hydrazone

- 163.0743
- 160.2664
- 152.7912
- 148.9591
- 148.6118
- 148.3697
- 140.6180
- 131.2157
- 129.3419
- 127.8107
- 127.2521
- 119.9533
- 108.4978
- 107.6330
- 105.6761

- 50.3165
- 49.8935

- 27.4730
- 21.5537
- 21.0802
- 20.1339
- 20.0942

