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Covalently Linked Rotaxane Encapsulation of a Benzil Core for Consistent Organic Room-Temperature Phosphorescence Across Diverse Solvents

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1. General Comments

Material: Unless otherwise stated, commercially available chemicals were used as received. Solvents were purified as follows: triethylamine was degassed by nitrogen bubbling before using. THF and DMF were purchased from Kanto Chemical and further purified by passage through activated alumina under positive nitrogen pressure as described by Grubbs et al.[1] Precursor **1** and 4,4'-bis(azidomethyl)biphenyl were synthesized according to previously reported procedures.[2, 3]

NMR Spectroscopy: ^{1}H NMR (500 MHz) and ^{13}C{^{1}H} NMR (126 MHz) were measured with a Bruker AVANCE-500 spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) in $CDCl_3$. The ^{13}C NMR chemical shifts are reported relative to $^{13}CDCl_3$ (77.16 ppm).

High-Resolution Mass Spectroscopy (HR-MS): Electrospray ionization time-of-flight (ESI-ToF) mass spectra were obtained using a Bruker micrOTOF II-KE02. The HR-MS spectra were internally calibrated using NaTFA clusters.

Preparative Recycling Gel Permeation Chromatography (GPC): Preparative recycling GPC was performed with a JAI LC9130NEXT System equipped with JAIGEL-2H or -2.5H columns, a JAI UV-370 NEXT, and a JAI RI-700 NEXT, or performed with a SHIMADZU LC-20AP System equipped with a Shodex K-4002.5L or K-4002L column, a SHIMADZU SPD-20A, and a SHIMADZU RID-10A using $CHCl_3$ as the eluent at a flow rate of 14 mL min^{-1}.

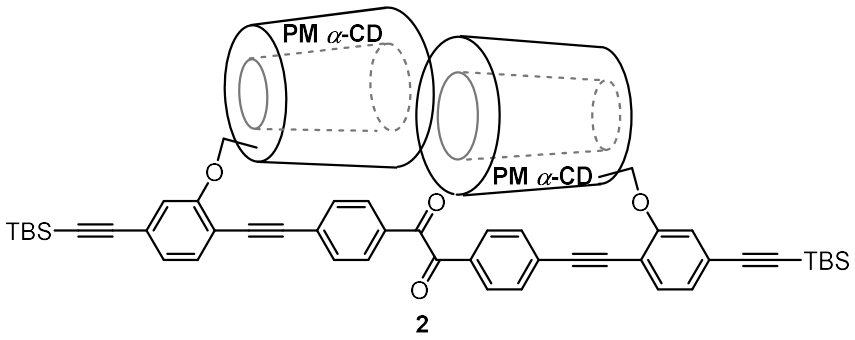
Absorption/Emission Spectra: Ultraviolet-visible absorption spectra were measured with a SHIMADZU UV-2600 model. Fluorescence spectra were measured on a SHIMADZU RF-6000 model.

Quantum Yield: Absolute quantum yields were determined by a calibrated integrating sphere system (Hamamatsu C13347). This system consists of an excitation light source, a sample holder mounted in an integrating sphere and a multi-channel CCD spectrometer.

Size Exclusion Chromatography: The analytical size-exclusion chromatography was performed with a GL-Science GL-7400 HPLC System equipped with Shodex KF-802, -803, -804 columns, a GL-7410 HPLC pump, a GL-7450 UV detector, and a GL-7454 RI detector using THF as the eluent at a flow rate of 0.6 mL/min. The molecular weights of polymers were determined using a calibration curve based on polystyrene.

2. Synthetic Procedures

2.1 Synthesis of 2



2

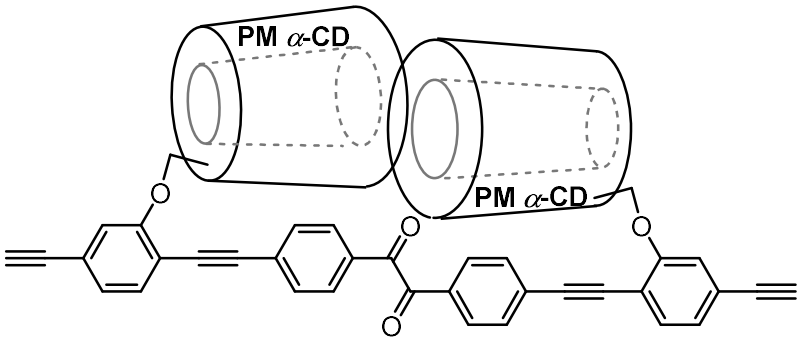
Precursor **1** (198.1 mg, 0.14 mmol), 4,4'-dibromobenzil (20.3 mg, 0.055 mmol), $Pd(PPh_3)_4$ (2.8 mg, 0.0024 mmol), $CuSO_4 \cdot 5H_2O$ (0.5 mg, 0.0031 mmol), and sodium ascorbate (1.1 mg, 0.0056 mmol) were added in a mixed solvent of NEt_3 (15 mL) and DMF (15 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 15 h, the solution was cooled to room temperature, extracted with EtOAc, dried over $MgSO_4$, and evaporated. The residue was purified by GPC with $CHCl_3$ as the eluent to yield **2** as a pale yellow solid (138.0 mg, 0.044 mmol, 81%).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 7.95 (d, J = 8.5 Hz, 4H, Ar*H*), 7.73 (d, J = 8.5 Hz, 4H, Ar*H*), 7.42 (d, J = 8.0 Hz, 2H, Ar*H*), 7.06 (d, J = 7.5 Hz, 2H, Ar*H*), 7.01 (s, 2H, Ar*H*), 5.30–3.00 (m, 186H, CD–*H*), 0.98 (s, 18H, SiCCH_3), 0.16 (s, 12H, SiCH_3).

^{13}C NMR (126 MHz; $CDCl_3$): δ = 193.21, 159.24, 133.40, 132.18, 132.02, 130.35, 130.01, 125.04, 124.81, 115.28, 112.77, 105.52, 100.60, 100.43, 100.37, 100.36, 100.33, 100.05, 94.93, 94.44, 91.04, 83.02, 82.76, 82.73, 82.70, 82.67, 82.65, 82.38, 82.33 (peaks overlapped), 82.13, 81.94, 81.38, 81.31 (peaks overlapped), 81.1, 72.01, 71.88, 71.74, 71.71 (peaks overlapped), 71.59, 71.46, 71.43, 71.36 (peaks overlapped), 70.6, 67.9, 62.02, 62.00 (peaks overlapped), 61.96 (peaks overlapped), 61.93, 59.45, 59.25 (peaks overlapped), 59.23, 59.21, 58.35, 58.06, 57.96 (peaks overlapped), 57.49, 26.24, 16.80, -4.51.

HR-MS (ESI-ToF-MS) *m/z*: $[M+2Na]^{2+}$ calcd. 1574.70838 for $C_{152}H_{230}Na_2O_{62}Si_2$, found 1574.70551.

2.2 Synthesis of 3-unenc



3-unenc

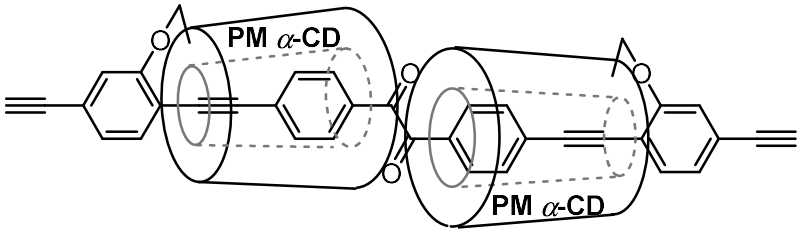
2 (138.0 mg, 0.044 mmol) and 1 M tetrabutylammonium fluoride in THF (0.12 mL, 0.12 mmol) were added in THF (2.5 mL) under a nitrogen atmosphere. After being stirred at room temperature for 15 min, the solution was quenched by HCl aq., extracted with $CHCl_3$, dried over $MgSO_4$, and evaporated. The residue was purified by GPC with $CHCl_3$ as the eluent to yield **3-unenc** as a pale yellow solid (61.4 mg, 0.021 mmol, 48%).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 7.96 (d, J = 8.4 Hz, 4H, Ar*H*), 7.74 (d, J = 8.4 Hz, 4H, Ar*H*), 7.44 (d, J = 7.9 Hz, 2H, Ar*H*), 7.09 (d, J = 7.9 Hz, 2H, Ar*H*), 7.05 (s, 2H, Ar*H*), 5.13–3.01 (m, 188H, CD–*H*, CC*H*).

^{13}C NMR (126 MHz; $CDCl_3$): δ = 193.15, 159.24, 133.42, 132.21, 132.08, 130.25, 130.00, 124.86, 123.91, 115.65, 113.22, 100.57, 100.35, 100.31, 100.27, 100.22, 99.92, 94.46, 90.75, 83.47, 83.00, 82.65 (peaks overlapped), 82.60, 82.33 (peaks overlapped), 82.31, 82.13, 81.94, 81.36, 81.34, 81.17, 79.10, 72.11, 71.88, 71.70, 71.63, 71.59, 71.43, 71.40, 71.37, 71.34, 70.62, 67.87, 61.98, 61.95 (peaks overlapped), 61.91, 61.86, 59.38 (peaks overlapped), 59.20, 59.16, 58.37, 58.06, 58.02, 57.97 (peaks overlapped), 57.50.

HR-MS (ESI-ToF-MS) *m/z*: $[M+2Na]^{2+}$ calcd. 1461.12361 for $C_{140}H_{202}Na_2O_{62}$, found 1461.12537.

2.3 Synthesis of 3-enc



3-enc

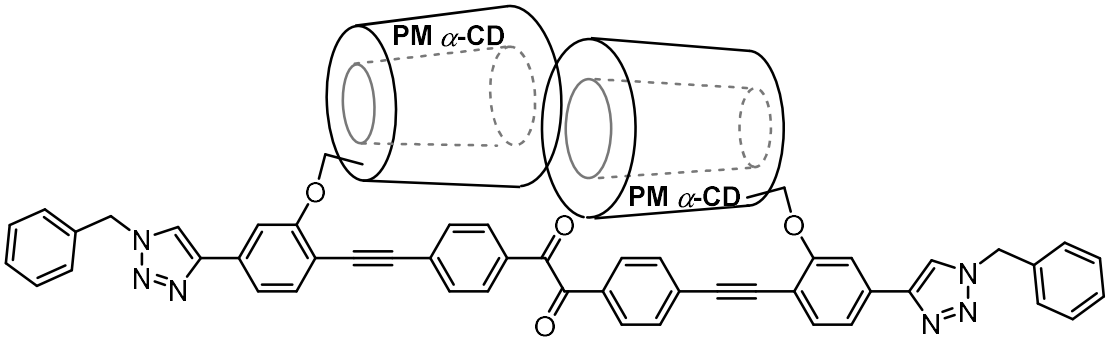
3-unenc (22.4 mg, 0.0078 mmol) was dissolved in MeOH (30 mL). The solution was stirred at 60 °C, and H_2O (30 mL) was added dropwise. After being stirred for 3 h, the solution was cooled to room temperature, extracted with $CHCl_3$, dried over $MgSO_4$, and evaporated. **3-enc** was yielded as a pale yellow solid (21.5 mg, 0.0075 mmol, 96%).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 8.29 (d, J = 8.5 Hz, 4H, Ar*H*), 8.24 (d, J = 8.6 Hz, 4H, Ar*H*), 7.54 (d, J = 8.3 Hz, 2H, Ar*H*), 7.30–7.28 (m, 4H, Ar*H*), 5.07–2.89 (m, 188H, CD–*H*, CC*H*)

^{13}C NMR (126 MHz; $CDCl_3$): δ = 187.70, 161.97, 133.54, 133.19, 132.81, 130.16, 128.29, 127.20, 125.76, 124.68, 117.08, 101.05, 100.81, 100.50, 100.39, 100.23, 98.51, 94.49, 91.05, 83.96, 83.28, 83.04, 82.65 (peaks overlapped), 82.59, 82.55, 82.52, 82.39, 82.35 (peaks overlapped), 82.32, 82.24, 82.20, 81.91 (peaks overlapped), 81.73, 81.56, 81.50, 81.47, 81.41, 81.35, 81.32, 81.28, 80.20, 72.15, 71.92, 71.81, 71.57, 71.49, 71.42, 70.75, 70.44, 61.93 (peaks overlapped), 61.69, 61.64, 61.60, 61.49, 61.48, 61.43, 59.40, 59.21, 59.17, 59.14, 59.04, 58.84, 58.78, 58.46, 58.10, 57.96 (peaks overlapped), 57.84, 57.79, 57.69.

HR-MS (ESI-ToF-MS) *m/z*: $[M+2Na]^{2+}$ calcd. 1461.12361 for $C_{140}H_{202}Na_2O_{62}$, found 1461.12518.

2.4 Synthesis of 4-unenc-cap



4-unenc-cap

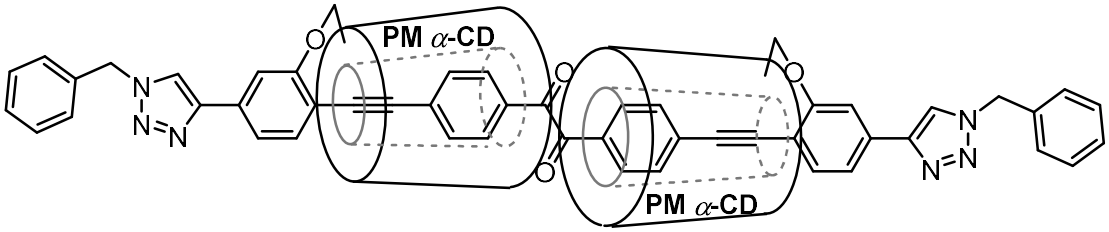
3-unenc (28.7 mg, 0.010 mmol), benzyl azide (30 μL, 0.24 mmol), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (4.1 mg, 0.0077 mmol), and $[Cu(CH_3CN)_4]BF_4$ (3.9 mg, 0.012 mmol) were added in the mixed solvent of *t*-BuOH (1 mL) and H_2O (1 mL). After being stirred for 8 h, the solution was extracted with $CHCl_3$, dried over $MgSO_4$, and evaporated. The residue was purified by GPC with $CHCl_3$ as the eluent to yield **4-unenc-cap** as a pale yellow solid (15.6 mg, 0.0050 mmol, 50%).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 7.95 (d, *J* = 8.6 Hz, 4H, Ar*H*), 7.74 (d, *J* = 8.6 Hz, 4H, Ar*H*), 7.71–7.70 (m, 4H, Ar*H*, C*H*), 7.48 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.38 (m, 6H, Ar*H*), 7.28 (dd, *J* = 7.4, 2.4 Hz, 4H, Ar*H*), 7.13 (dd *J* = 7.9, 1.4 Hz, 2H, Ar*H*), 5.58 (m, 4H, CH_2), 5.16–3.01 (m, 186H, CD–*H*).

^{13}C NMR (126 MHz; $CDCl_3$): δ = 193.29, 160.16, 147.59, 134.59, 133.97, 132.69, 132.15, 131.92, 130.56, 130.01, 129.36, 129.09, 128.11, 120.17, 117.99, 111.97, 109.09, 100.58, 100.39, 100.31, 100.27, 100.04, 93.67, 91.42, 82.67, 82.65, 82.59, 82.57, 82.51, 82.38, 82.33 (peaks overlapped), 82.14, 81.91, 81.47, 81.37 (peaks overlapped), 81.24, 71.83, 71.64, 71.46 (peaks overlapped), 71.43, 70.65, 67.83, 61.99 (peaks overlapped), 61.94, 61.88, 59.48, 59.24 (peaks overlapped), 59.21, 58.85, 58.35, 58.07, 57.96, 57.48, 54.50.

HR-MS (ESI-ToF-MS) *m/z*: $[M+2Na]^{2+}$ calcd. 1594.18756 for $C_{154}H_{216}Na_2O_{62}$, found 1594.18909.

2.5 Synthesis of 4-enc-cap



4-enc-cap

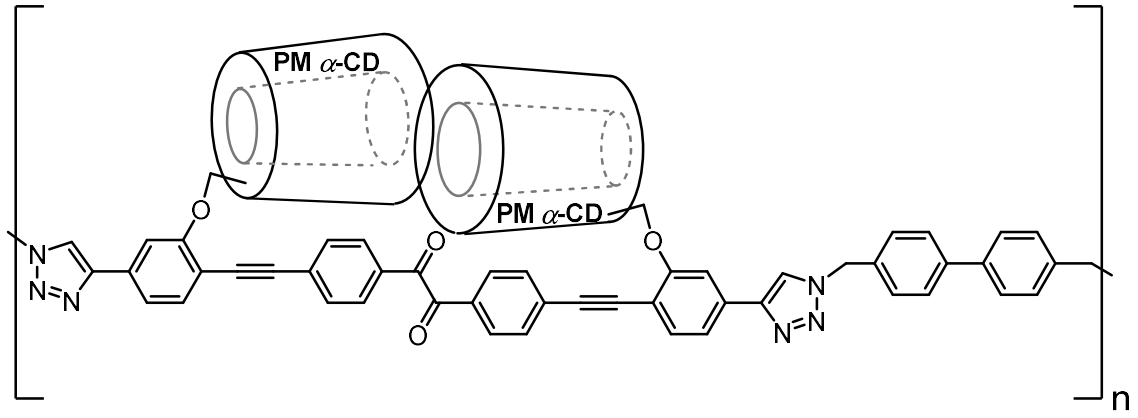
3-enc (56.3 mg, 0.020 mmol), benzyl azide (60 μL, 0.48 mmol), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (3.2 mg, 0.0060 mmol), $[Cu(CH_3CN)_4]BF_4$ (4.7 mg, 0.0150 mmol) were added in the mixed solvent of *t*-BuOH (3 mL) and H_2O (3 mL). After being stirred for 8 h, the solution was extracted with $CHCl_3$, dried over $MgSO_4$, and evaporated. The residue was purified by GPC with $CHCl_3$ as the eluent to yield **4-enc-cap** as a pale yellow solid (30.2 mg, 0.0098 mmol, 49%).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 8.29 (d, J = 8.2 Hz, 4H, Ar*H*), 8.24 (d, J = 8.2 Hz, 4H, Ar*H*), 7.73 (m, 4H, Ar*H*, *CH*), 7.59 (d, J = 8.0 Hz, 2H, Ar*H*), 7.53 (s, 2H, Ar*H*), 7.42 (m, 6H, Ar*H*), 7.35-7.34 (m, 4H, Ar*H*), 5.60 (s, 4H, CH_2), 5.06-2.84 (m, 186H, CD–*H*).

^{13}C NMR (126 MHz; $CDCl_3$): δ = 187.74, 162.73, 146.90, 134.46, 133.98, 133.34, 133.06, 132.75, 130.15, 129.43, 129.18, 128.53, 128.32, 120.72, 120.17, 119.30, 115.67, 101.08, 100.82, 100.49, 100.39, 100.27, 98.51, 93.65, 91.52, 84.01, 83.15, 82.96, 82.60, 82.57, 82.55 (peaks overlapped), 82.32, 82.26, 82.21, 81.86, 81.75, 81.58, 81.52, 81.49, 81.35, 81.29, 72.46, 72.15, 71.94, 71.85, 71.54, 71.43, 71.40 (peaks overlapped), 70.74, 70.70, 70.35, 61.69, 61.65, 61.61, 61.51, 61.48, 61.43 (peaks overlapped), 59.23 (peaks overlapped), 59.08, 58.86, 58.82, 58.44, 58.10, 57.95, 57.84, 57.80, 57.67, 54.61.

HR-MS (ESI-ToF-MS) *m/z*: $[M+2Na]^{2+}$ calcd. 1594.18756 for $C_{154}H_{216}Na_2O_{62}$, found 1594.18567.

2.6 Synthesis of 5-unenc

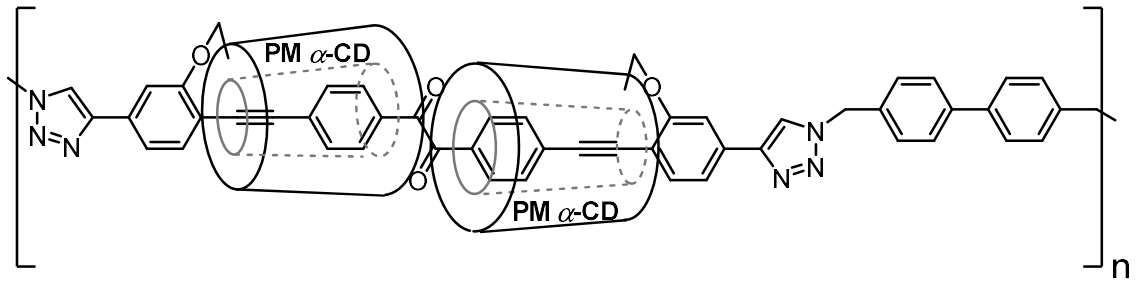


5-unenc

3-unenc (6.0 mg, 0.0020 mmol), 4,4'-bis(azidomethyl)biphenyl (0.47 mg, 0.0018 mmol), $CuSO_4 \cdot 5H_2O$ (0.1 mg, 0.0004 mmol), and sodium ascorbate (0.1 mg, 0.0005 mmol) were added in the mixed solvent of DMSO (1 mL) and H_2O (0.2 mL). After being stirred for 8 h, the solution was extracted with $CHCl_3$, dried over $MgSO_4$, and evaporated. The residue was purified by GPC with $CHCl_3$ as the eluent to yield **5-unenc** as a pale yellow solid (3.3 mg).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 7.96 (d, 4H, Ar*H*), 7.77-7.73 (m, 8H, Ar*H*, C*H*), 7.77 (d, 4H, Ar*H*), 7.48 (d, 2H, Ar*H*), 7.36 (d, 4H, Ar*H*), 7.11 (m, 2H, Ar*H*), 5.62 (m, 4H, CH_2), 5.17–2.99 (m, 186H, CD–*H*).

2.7 Synthesis of 5-enc



5-enc

3-enc (13.4 mg, 0.0047 mmol), 4,4'-bis(azidomethyl)biphenyl (1.2 mg, 0.0045 mmol), $CuSO_4 \cdot 5H_2O$ (0.2 mg, 0.0008 mmol), and sodium ascorbate (0.2 mg, 0.001 mmol) were added in the mixed solvent of DMSO (1 mL) and H_2O (0.2 mL). After being stirred for 8 h, the solution was extracted with $CHCl_3$, dried over $MgSO_4$, and evaporated. The residue was purified by GPC with $CHCl_3$ as the eluent to yield **5-enc** as a pale yellow solid (11.0 mg).

^{1}H NMR (500 MHz; $CDCl_3$): δ = 8.30 (d, 4H, Ar*H*), 8.24 (d, 4H, Ar*H*), 7.80 (s, 2H, *CH*), 7.74 (d, 2H, Ar*H*), 7.60 (m, 6H, Ar*H*), 7.54 (s, 2H, Ar*H*), 7.42 (d, 4H, Ar*H*), 5.64 (s, 4H, CH_2), 5.08-2.83 (m, 186H, CD–*H*).

3. NMR Spectra

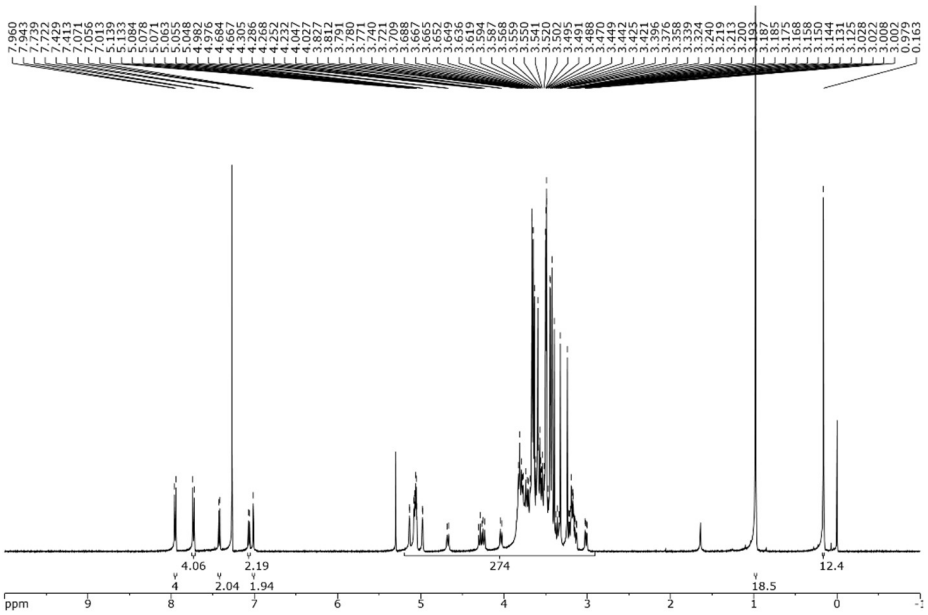


Figure S1. ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$).

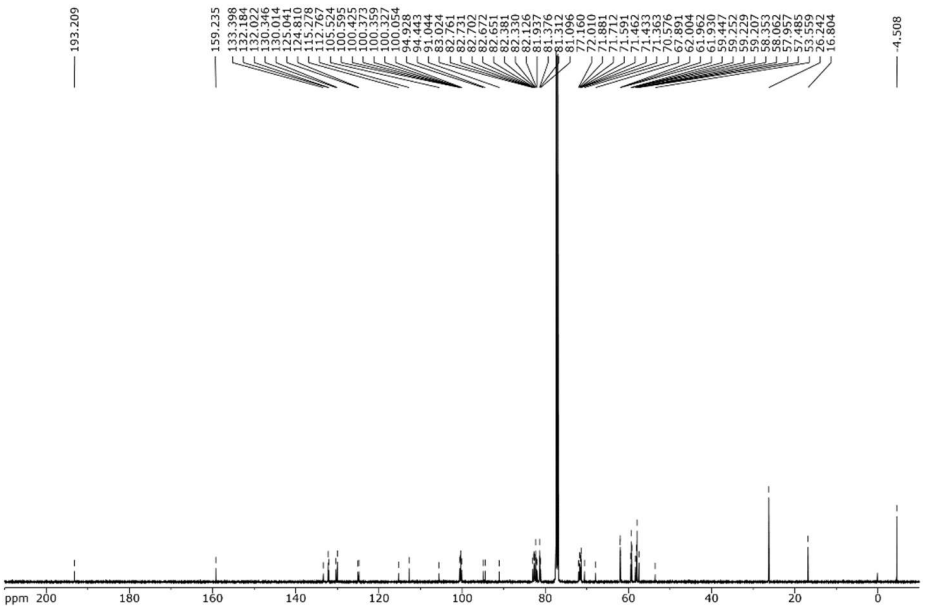


Figure S2. ^{13}C NMR spectrum of **2** (500 MHz, $CDCl_3$).

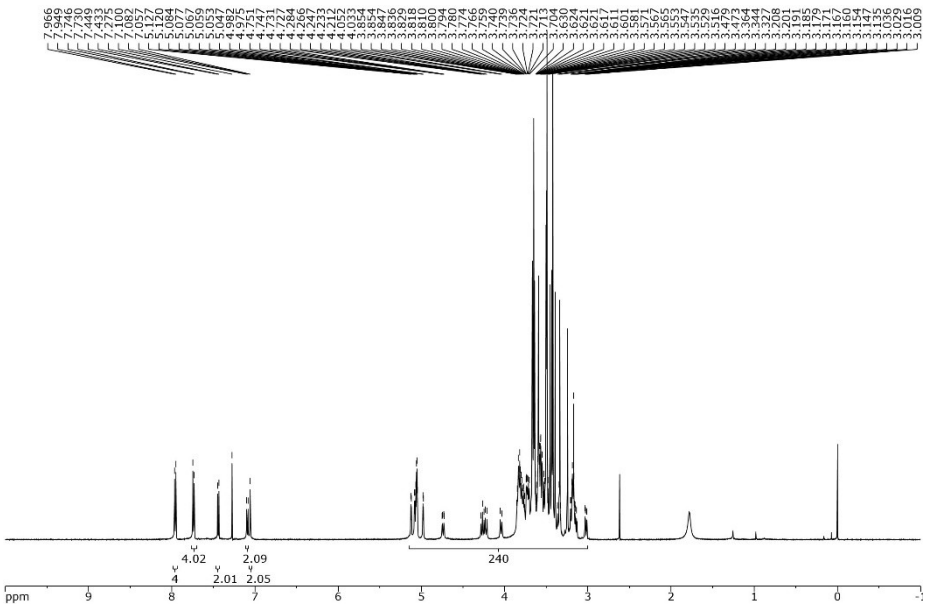


Figure S3. ^{1}H NMR spectrum of **3-unenc** (500 MHz, $CDCl_3$).

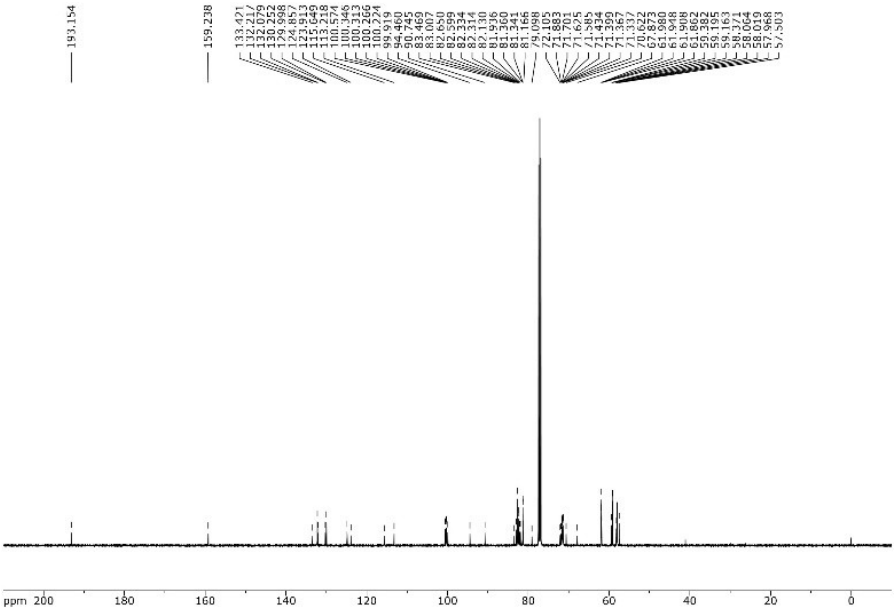


Figure S4. ^{13}C NMR spectrum of **3-unenc** (126 MHz, $CDCl_3$).

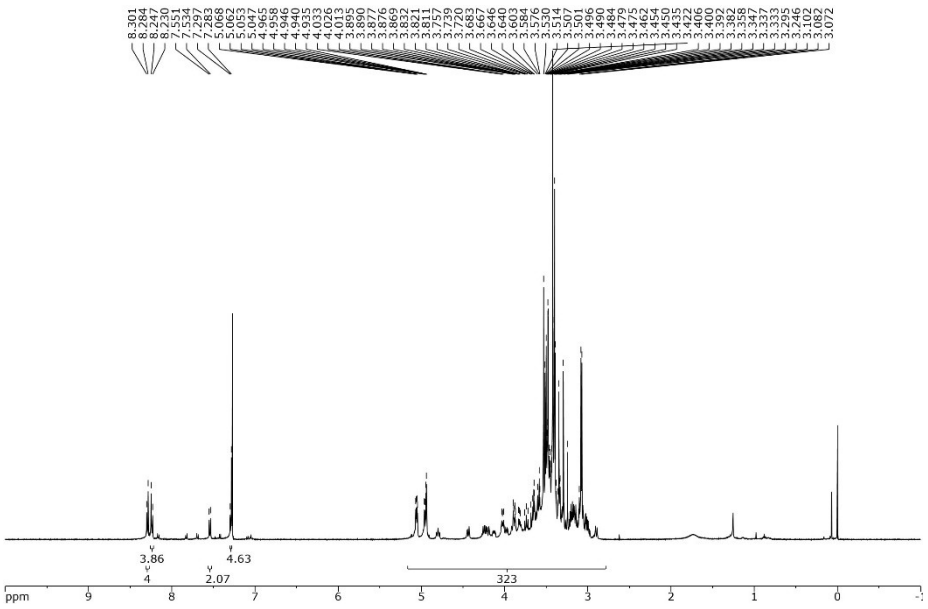


Figure S5. ^{1}H NMR spectrum of **3-enc** (500 MHz, $CDCl_3$).

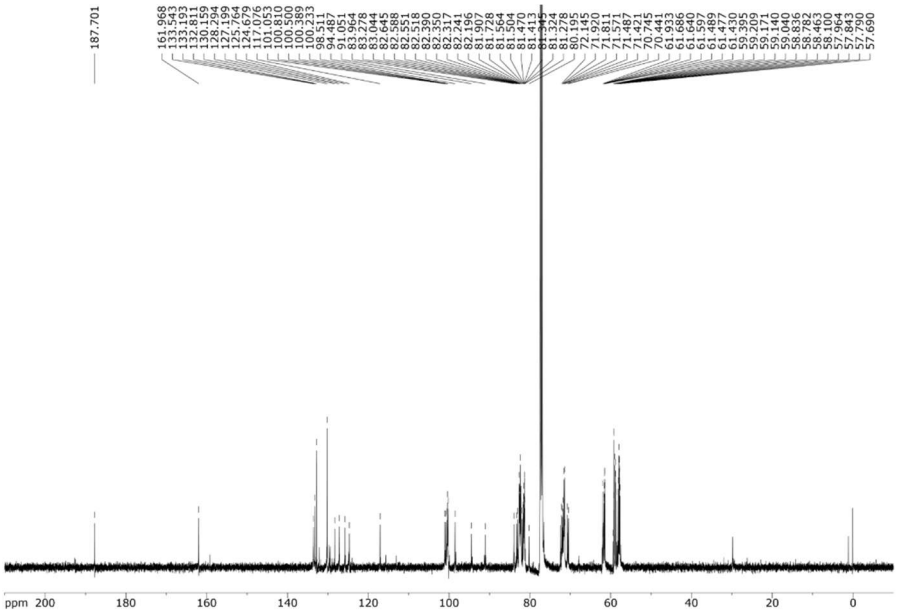


Figure S6. ^{13}C NMR spectrum of **3-enc** (126 MHz, $CDCl_3$).

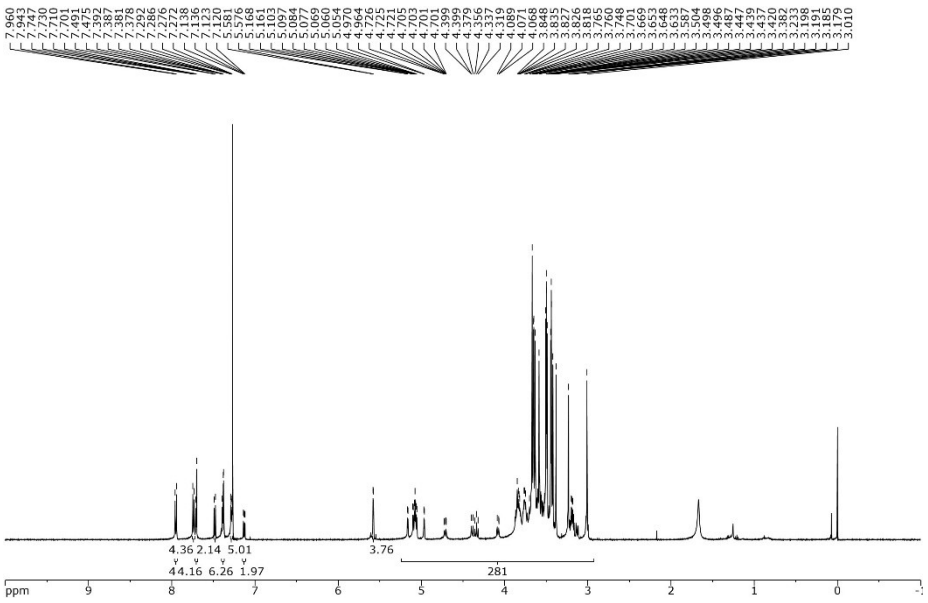


Figure S7. ^{1}H NMR spectrum of **4-unenc-cap** (500 MHz, $CDCl_3$).

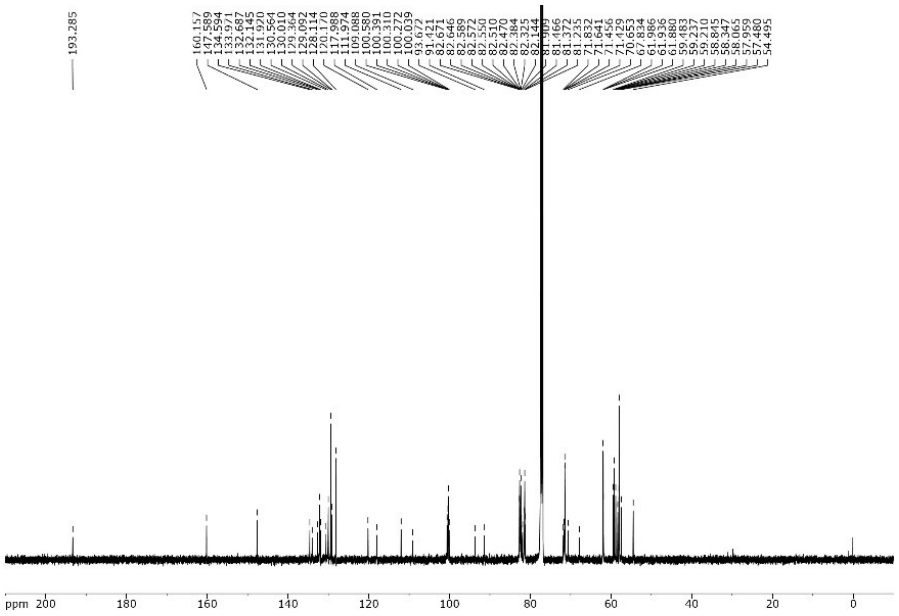


Figure S8. ^{13}C NMR spectrum of **4-unenc-cap** (126 MHz, $CDCl_3$).

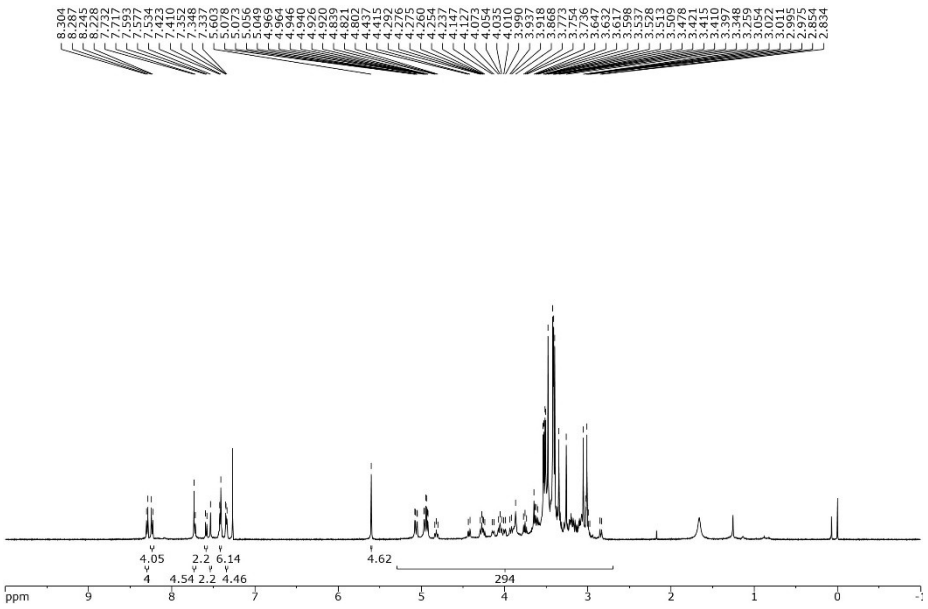


Figure S9. ^{1}H NMR spectrum of **4-enc-cap** (500 MHz, $CDCl_3$).

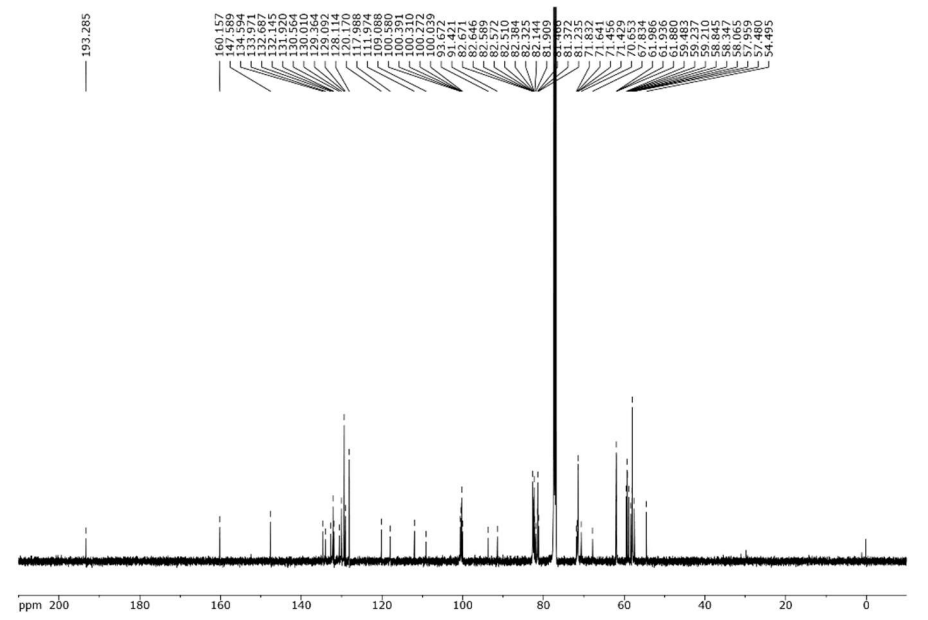


Figure S10. ^{13}C NMR spectrum of **4-enc-cap** (126 MHz, $CDCl_3$).

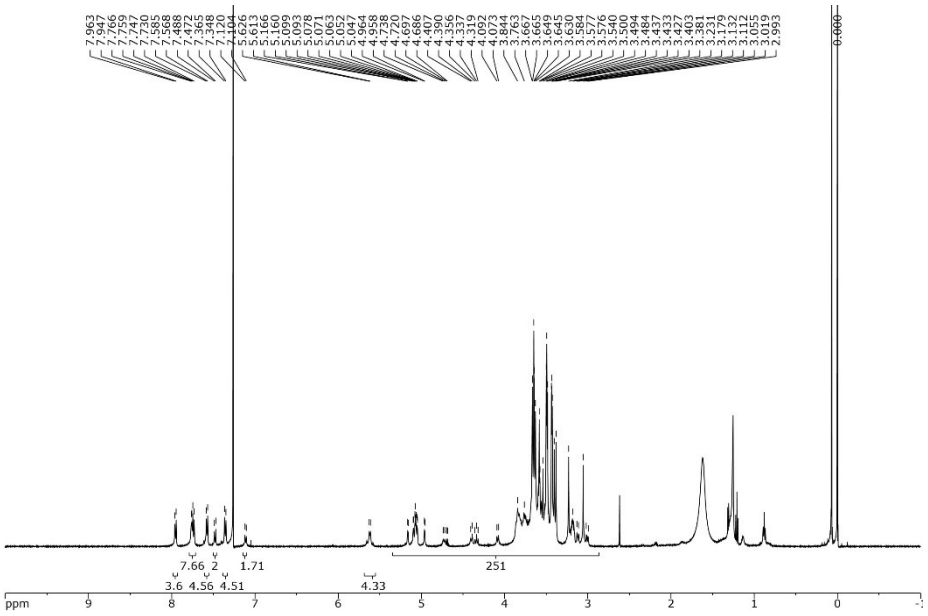


Figure S11. ^{1}H NMR spectrum of **5-unenc** (500 MHz, $CDCl_3$).

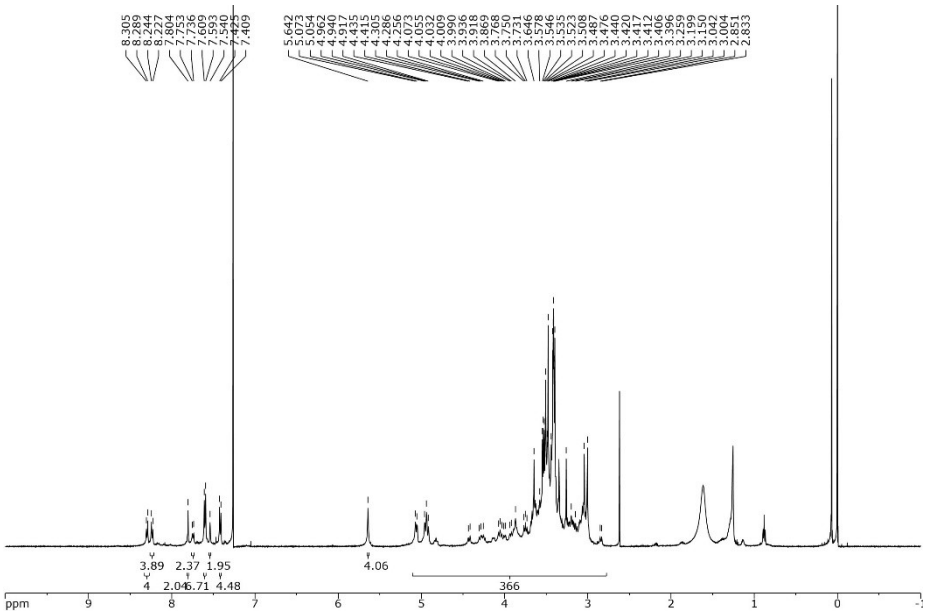


Figure S12. ^{1}H NMR spectrum of **5-enc** (500 MHz, $CDCl_3$).

4. ESI-ToF-MS Spectra

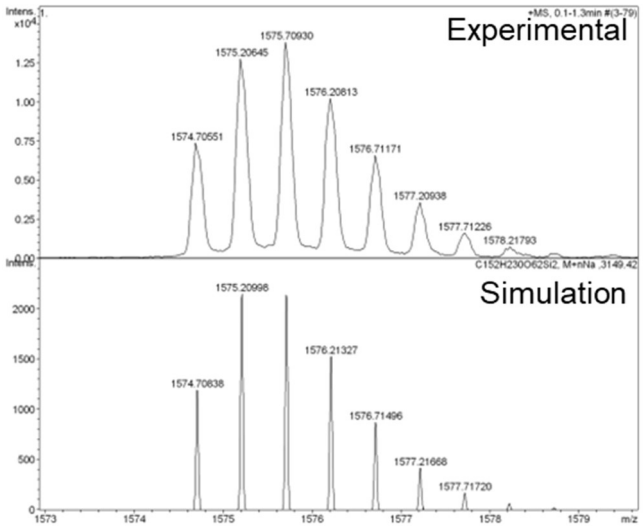


Figure S13. ESI-ToF-MS spectrum of **2**

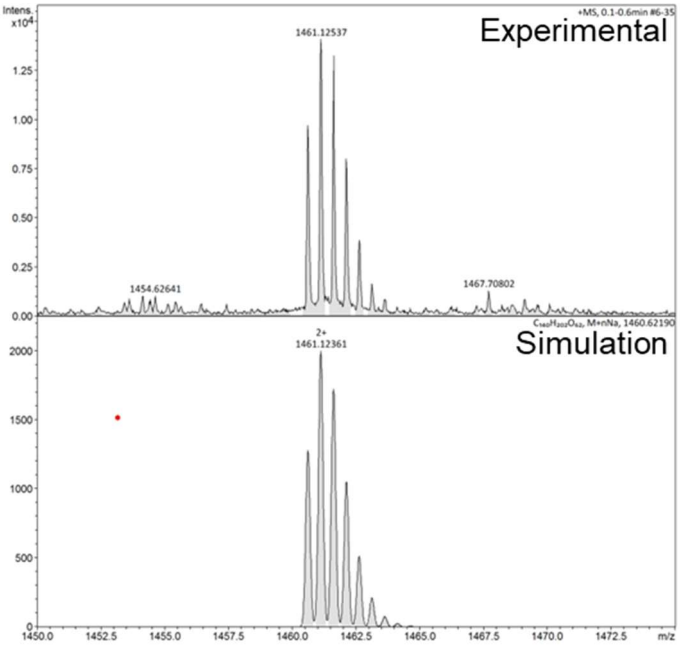


Figure S14. ESI-ToF-MS spectrum of **3-unenc**

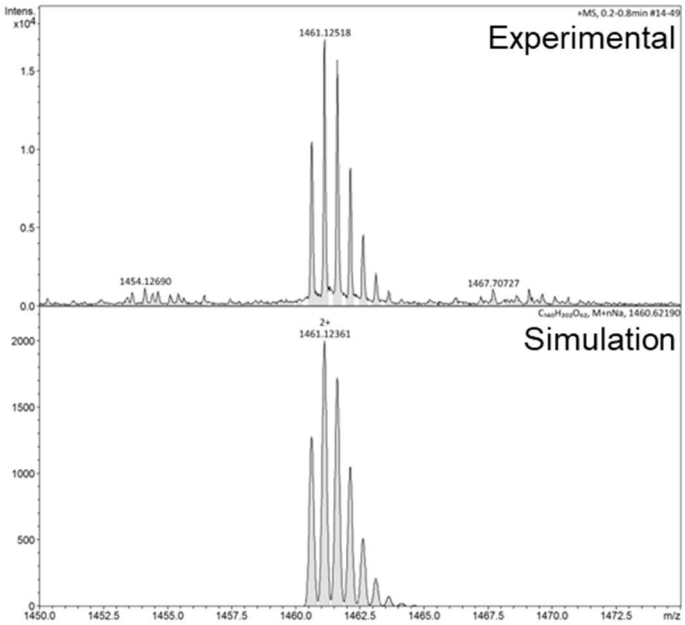


Figure S15. ESI-ToF-MS spectrum of **3-enc**

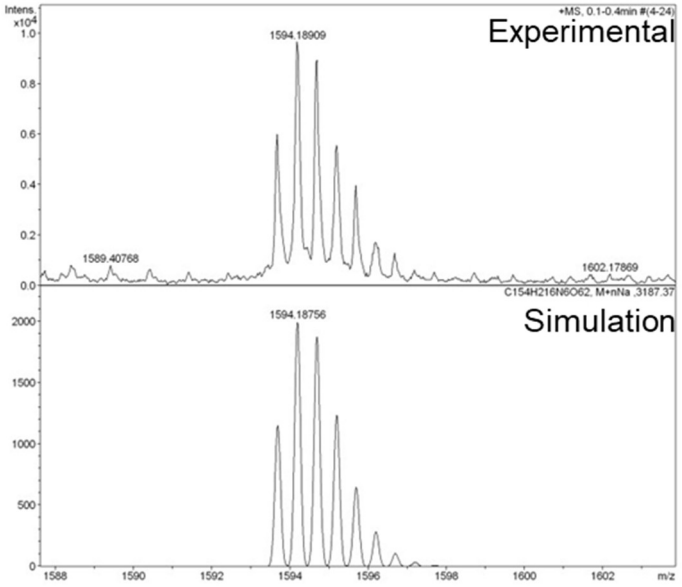


Figure S16. ESI-ToF-MS spectrum of **4-unenc-cap**

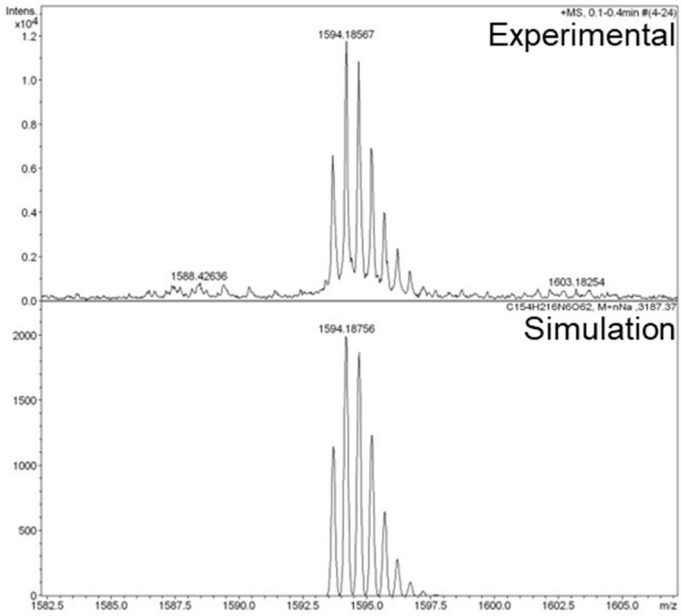


Figure S17. ESI-ToF-MS spectrum of **4-enc-cap**

5. Optical Analysis

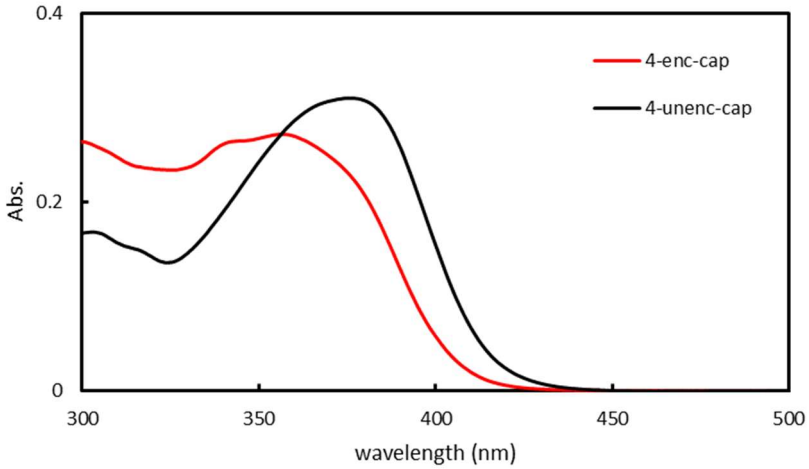


Figure S18. Absorption spectra of **4-enc-cap** and **4-unenc-cap** in $CHCl_3$ after nitrogen bubbling for 30 minutes. (concentration: 1×10^{-5} mol/L)

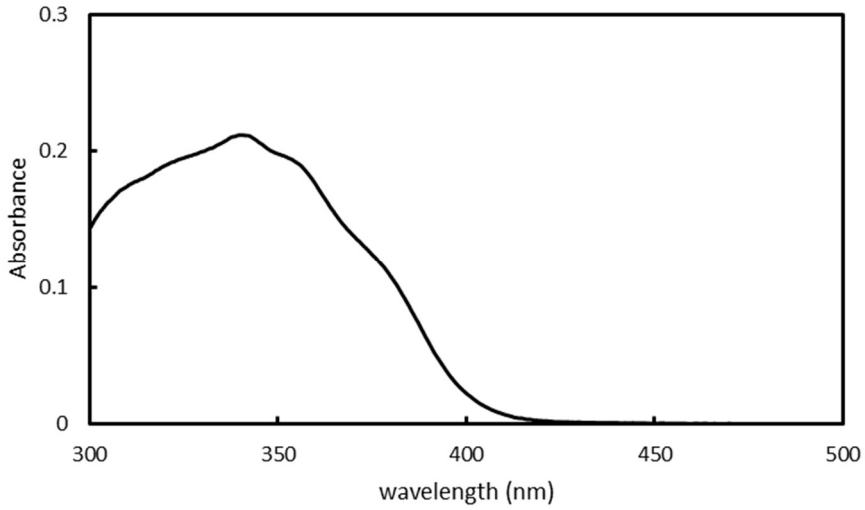


Figure S19. Absorption spectrum of **4-enc-cap** in toluene after nitrogen bubbling for 30 minutes. (concentration: 1×10^{-5} mol/L)

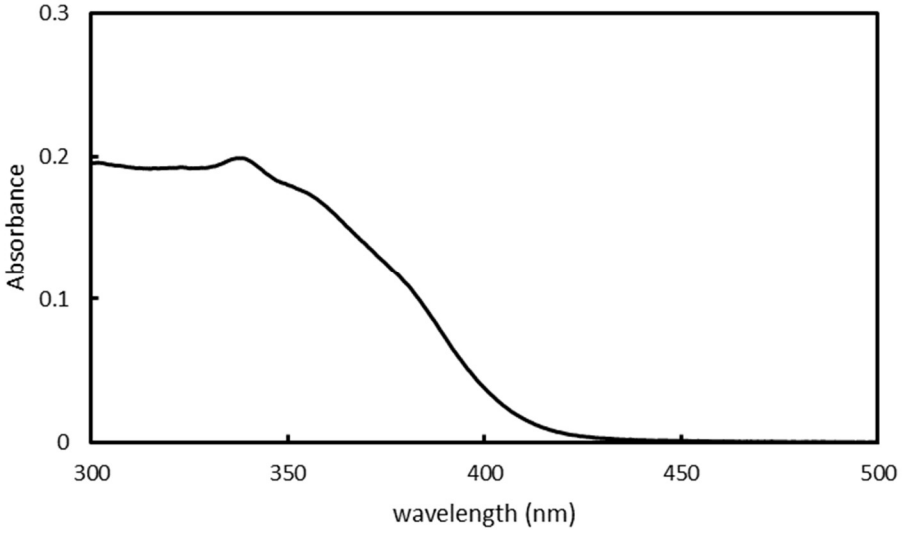


Figure S20. Absorption spectrum of **4-enc-cap** in MeCN after nitrogen bubbling for 30 minutes. (concentration: 1×10^{-5} mol/L)

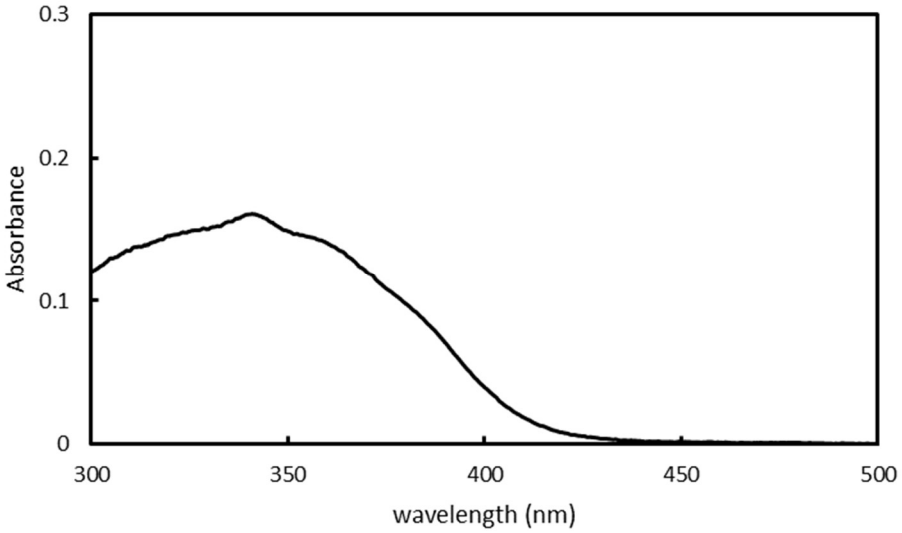


Figure S21. Absorption spectrum of **4-enc-cap** in DMSO after nitrogen bubbling for 30 minutes. (concentration: 1×10^{-5} mol/L)

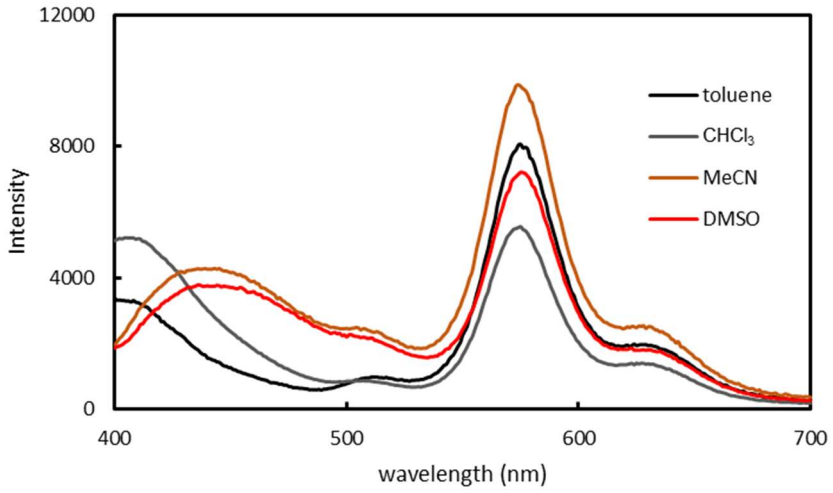


Figure S22. Emission spectra of **4-enc-cap** in toluene, MeCN after nitrogen bubbling for 10 minutes. (concentration: 1×10^{-5} mol/L, excitation: 365 nm)

6. Size Exclusion Chromatography

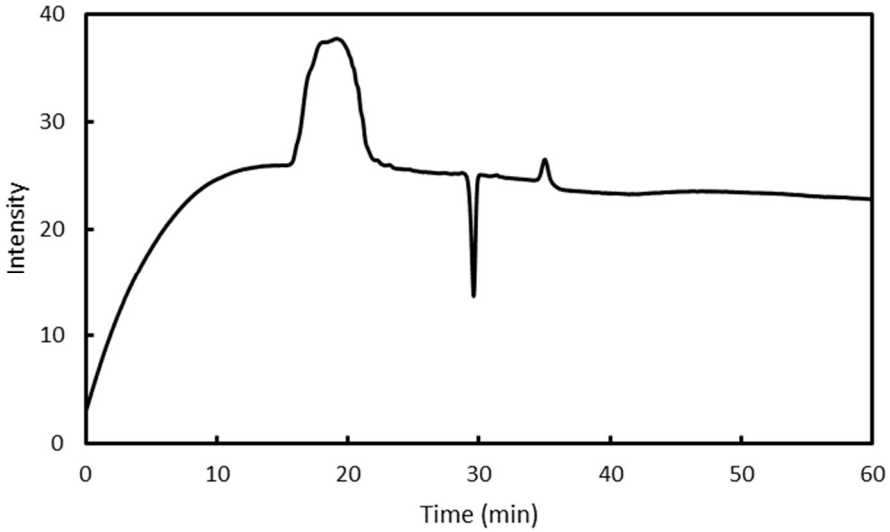


Figure S23. Size exclusion chromatography of **5-enc** after purification
(The molecular weight of **5-enc** is estimated to be around 40,000)

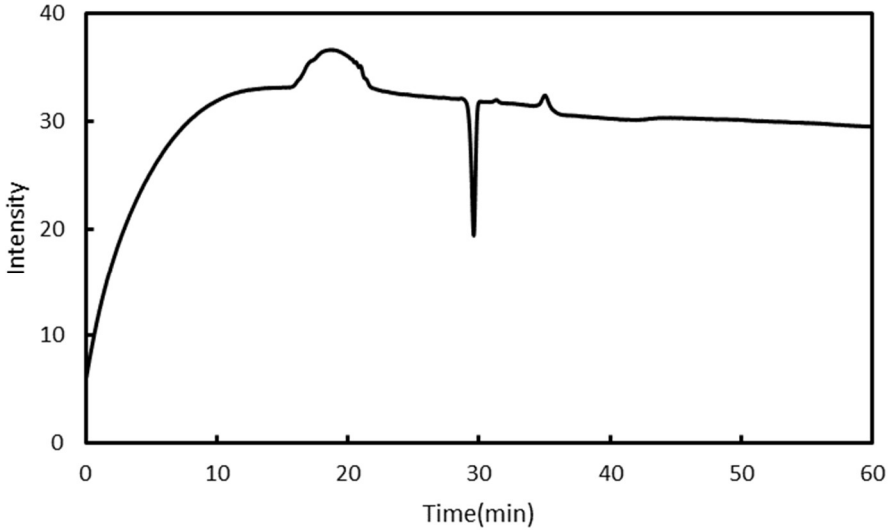


Figure S24. Size exclusion chromatography of **5-unenc** after purification
(The molecular weight of **5-unenc** is estimated to be around 40,000)

7. References

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3 M. Pascu, A. Ruggi, R. Scopelliti, K. Severin, *Chem. Commun.* 2013, **49**, 45.