

Supporting information

Synthesis of a Luminescent Lariat Aza-Crown Ether by Huisgen Cycloaddition

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1. General methods

Analytical control of the synthesized compounds was done by common methods. Melting points were determined on Büchi SMP or a Lambda Photometrics OptiMelt MPA 100 and are uncorrected. IR Spectra were recorded with a Bio-Rad FT-IR Excalibur FTS 3000. UV spectra were recorded on a Cary 50 BIO spectrometer with temperature control at 25°C. Electro spray mass spectra were performed on a Finnigan MAT TSQ 7000 ESI-spectrometer. Other Mass Spectra were recorded on Varian CH-5 (EI), Finnigan MAT 95 (CI; FAB and FD), Xenon serves as the ionization gas for FAB. NMR spectra were recorded on Bruker Avance 600 (^1H : 600.1 MHz, ^{13}C : 150.1 MHz, T = 300 K), Bruker Avance 400 (^1H : 400.1 MHz, ^{13}C : 100.6 MHz, T = 300 K) or Bruker Avance 300 (^1H : 300.1 MHz, ^{13}C : 75.5 MHz, T = 300 K) relative to external standards. NMR spectra were recorded in CDCl_3 at 300 MHz (^1H) or 75 MHz (^{13}C) unless stated otherwise. Characterization of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dd = double doublet, dt = double triplet, ddd = double double doublet. Integration is determined as the relative number of atoms, the coupling constants are given in Hertz [Hz]. The multiplicity of the carbon atoms is given as (+) = CH_3 or CH, (-) = CH_2 and (C_{quat}) for quaternary carbon atoms. Structural assignments are based on DEPT and COSY experiments where applicable. Error of reported values: chemical shift: 0.01 ppm for ^1H -NMR, 0.1 ppm for ^{13}C -NMR and 0.1 Hz for coupling constants. The solvent used is reported for each spectrum.

Analytical TLC plates (silica gel 60 F₂₅₄) and silica gel 60 (70 - 230 or 230 - 400 mesh) were used for chromatographic separations. Visualization of the spots was by UV light and/or staining with phosphomolybdate or ninhydrin, both in ethanol. DMF, CH_3CN , CHCl_3 , THF, and Et_2O were dried by standard procedures and stored over molecular sieves. PE means petrol ether with a boiling range of 70 - 90 °C. All other solvents and chemicals were of reagent grade and used with out further purification. All test substances were of pro analysi grade, checked by NMR or HPLC and used as purchased with out further purification.

Solvents for fluorescence measurements were from special spectroscopic purity purchased from Acros or Baker or Uvasol from Merck. Millipore water (18 M Ω , Milli Q_{Plus}) was used.

2. ^1H – and ^{13}C -NMR spectra of the new compound

NMR spectra were recorded in CDCl_3 on a Bruker Avance spectrometer 300 at 300 K. TMS was used as external standard.

Figure S-1: ^1H -NMR spectrum of compound **3**

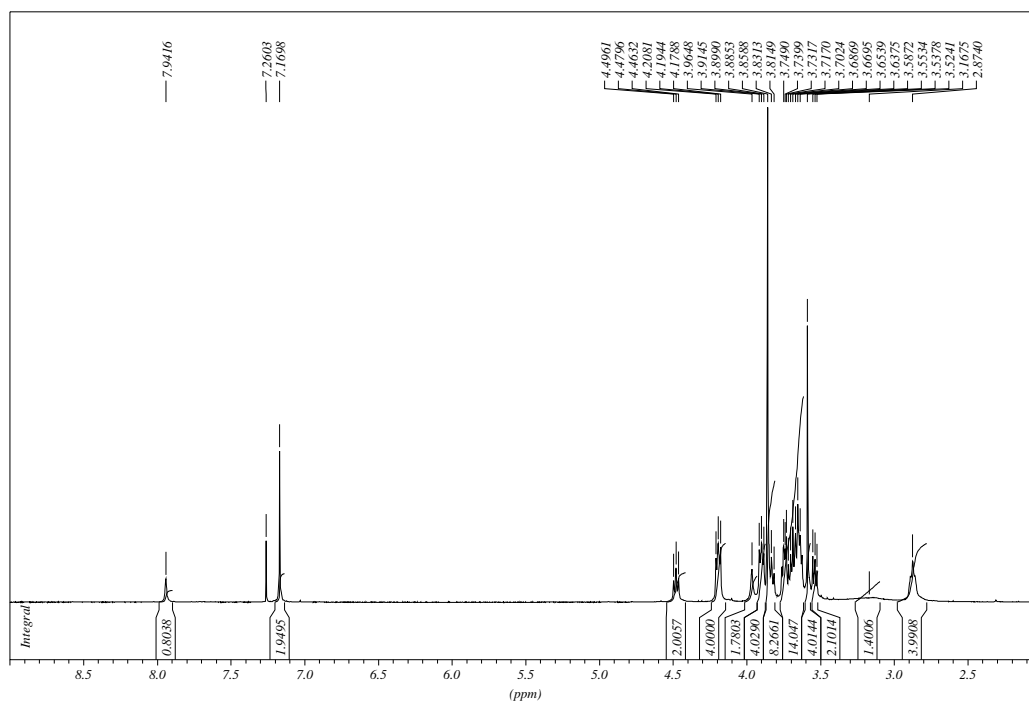
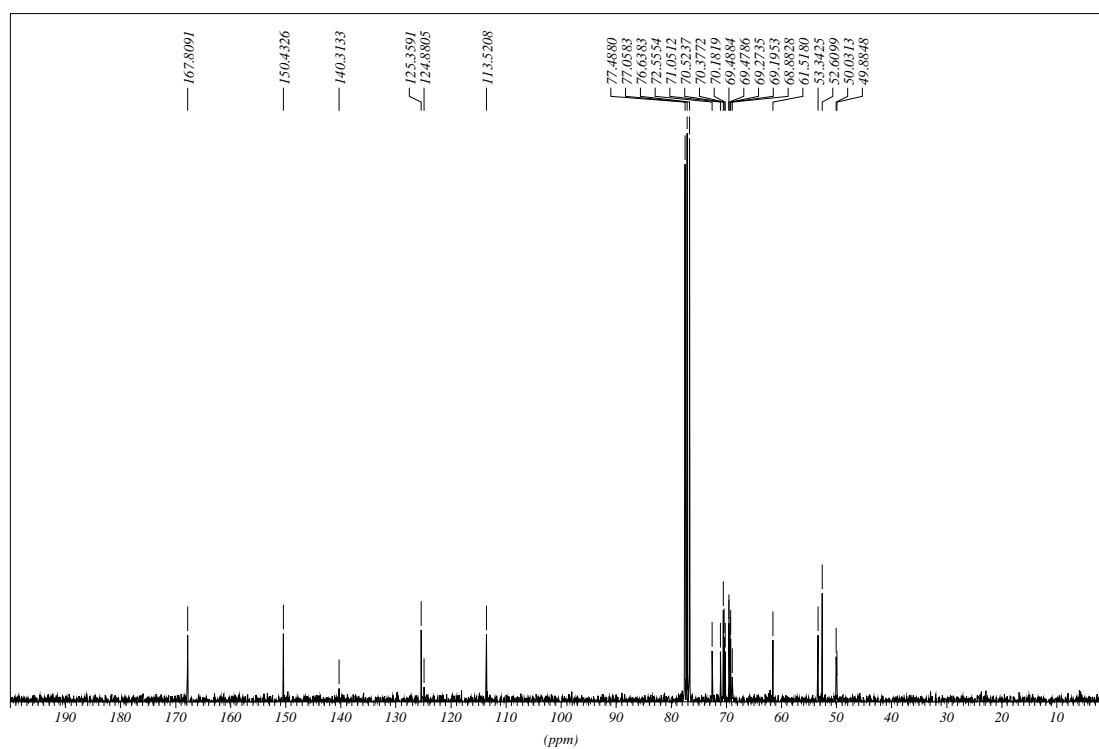
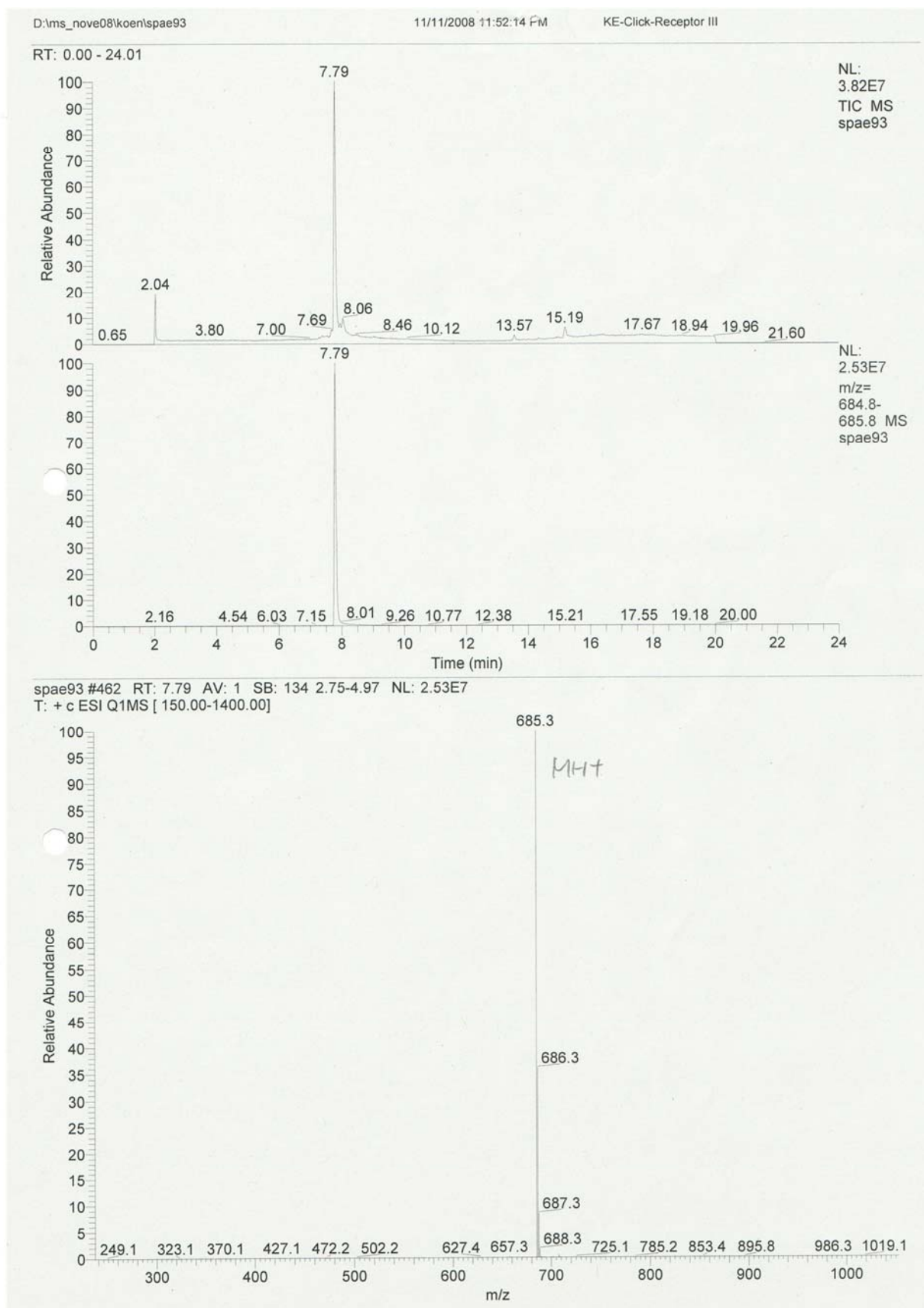


Figure S-2: ^{13}C -NMR spectrum of compound **3**



3. LC-MS spectrum of compound 3

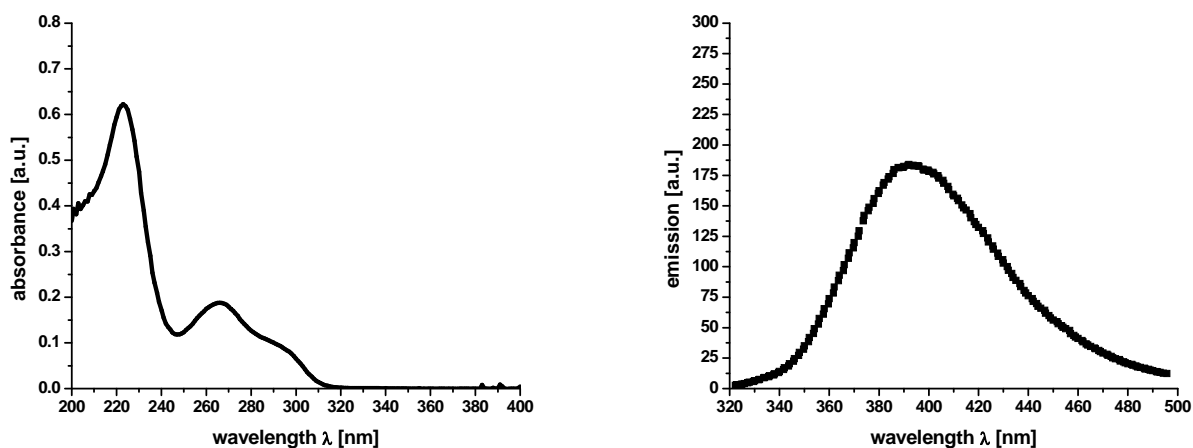
Figure S-3: LC-MS spectrum of compound 3



4. Absorption and emission spectra

Compound **3** shows absorption maxima in methanol at 225 nm and 270 nm, and emits upon excitation at 390 nm (see figure S-4) with a quantum yield of about $\phi = 0.1$. [1]

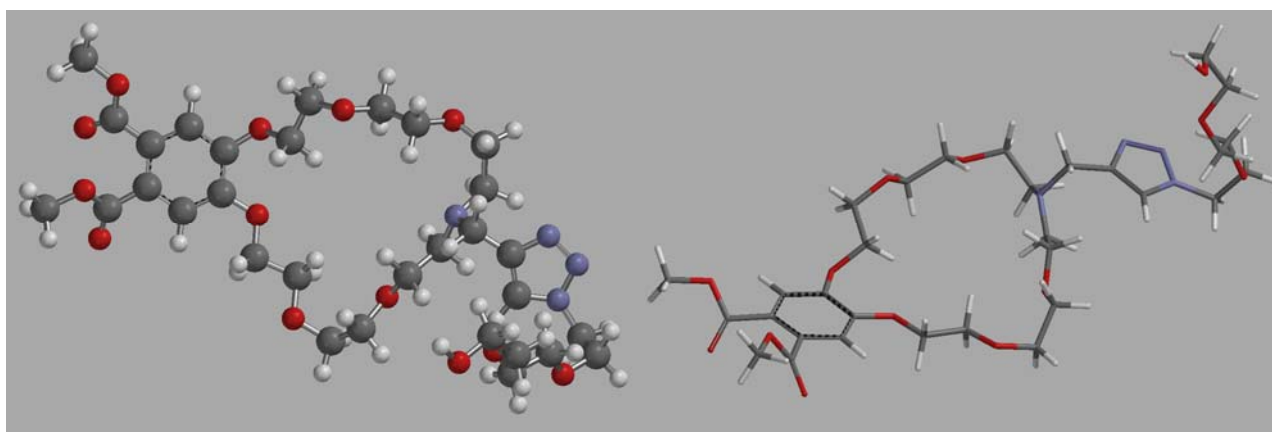
Figure S-4: Absorption and emission spectra of compound **3** ($c = 2.1 \cdot 10^{-5}$ mol/L) in methanol



5. Energy minimization calculations with Spartan V.6.01

Molecular models of the lowest energy conformers of both compounds were obtained by force field methods with the SPARTAN program package:

Figure S-5: Energy minimized structure of compound **3**



References and Notes

1. All quantum yields were determined with quinine disulfate in 1 N H₂SO₄ as the reference compound ($\Phi = 0.546$). The solution was degassed and measured in a closed, nitrogen flushed cuvette with septum.

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