

Hydrogen-Bonded Perylene/Terthiophene-Materials: Synthesis and Spectroscopic Properties

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Contents

S1-Chlorination reaction of compound 3	S2
S2-Characterization of compound 5	S4
S3-Characterization of compound 1a	S5
S4-Characterization of compound 1b	S5
S5-Characterization of compound 1c	S7
S6-Characterization of compound 2a	S8
S7-Characterization of compound 2b	S9

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S1- Chlorination reaction of compound 3

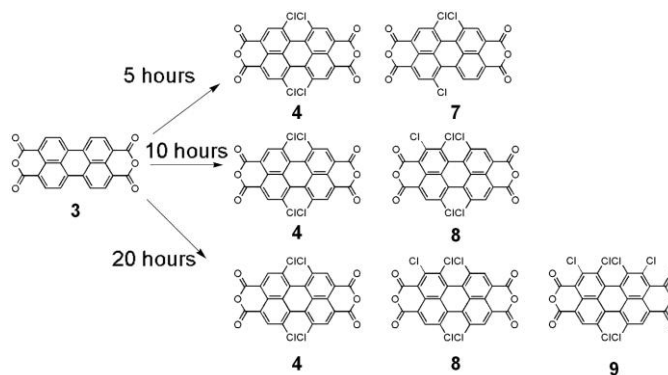
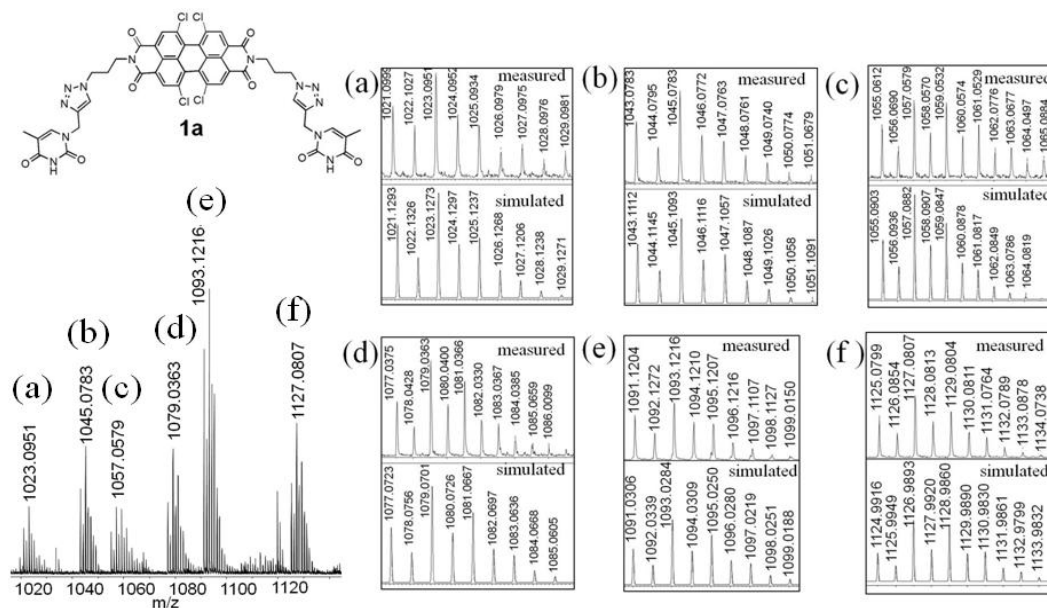


Figure S1. Chlorination reaction of **3** in different reaction times

The product of the chlorination reaction was purified by soxhlet extraction with dichloromethane as solvent, however the poor solubility of this product (**4**) did not allow characterization with NMR spectroscopy or mass spectrometry.



Therefore the definition of the number of the chlorine atoms was only possible after reaction to a soluble product like **1a**, **b**, **c** or elemental analysis of the insoluble product (**4**). A first try for this reaction was done according to the literature¹ in 20 hours at 70°C in chlorosulfonic acid and iodine. For investigations of the attached number of chlorines further steps of the reaction were conducted by reaction of **4** with 3-azidopropylamine in toluene under reflux to yield **5** and subsequent transformation of **5** via the azide /alkyne- “click”- reaction to yield the soluble product **1a**. The resulting product was characterized by ¹H-NMR spectroscopy and ESI-TOF- mass spectrometry. The ESI-TOF-MS spectrum indicated a mixture of products substituted with 4-, 5- and 6- chlorine atoms as indicated by six main peaks (see Figure S2). The peak at 1023.12 Da was simulated for the product with 4 chlorines as proton adduct ($[C_{46}H_{32}Cl_4N_{12}O_8+H]^+$); the peak at 1045.07 Da was simulated again for 4 chlorine atoms as sodium adduct ($[C_{46}H_{32}Cl_4N_{12}O_8+Na]^+$). Two peaks at 1057.05 Da and 1079.03 Da were simulated for the product with five substituted chlorines as proton ($[C_{46}H_{31}Cl_5N_{12}O_8+H]^+$) and sodium adduct ($[C_{46}H_{31}Cl_5N_{12}O_8+Na]^+$). Finally, the peak at 1093.12 Da was simulated for five substituted chlorine as a biradical species ($[C_{46}H_{29}Cl_5N_{12}O_8+K]^+$), the peak at 1127.08 Da was simulated with six chlorine atoms as a biradical species. ($[C_{46}H_{28}Cl_6N_{12}O_8+K]^+$).

Therefore it was decided to decrease the reaction time of the chlorination by reacting for 10 hours. This time, before continuing the other steps of the reaction, the number of the chlorine atoms was investigated by elemental analysis and was shown that the product contained approximately 4 chlorine atoms (Measured: 26.84-26.73%, Calculated: 26.75). Again, this product was treated with 3-azidopropylamine and subsequently transformed to **1a** via the azide/alkyne click reaction.

ESI-TOF-MS showed that it still contained some product with five chlorine atoms. The mass spectrum (Figure S3) showed two main peaks at 1045.11 Da which was simulated for the product with four chlorine atoms as sodium adduct ($[C_{46}H_{32}Cl_4N_{12}O_8+Na]^+$) and 1093.16 Da was simulated for five substituted chlorine as a biradical species ($[C_{46}H_{29}Cl_5N_{12}O_8+K]^+$). This result showed that elemental analysis is not an exact measurement for determination of the number of chlorine atoms

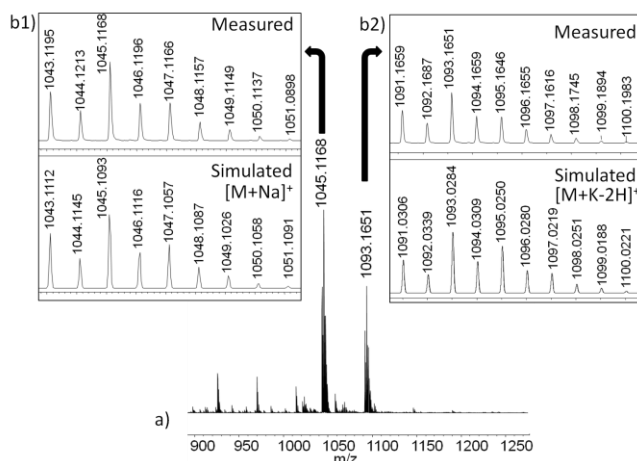


Figure S3. a) ESI-TOF-MS spectrum of compound **1a** b) measured and simulated isotopic pattern of **1a**
 1) ($M = C_{46}H_{32}Cl_4N_{12}O_8$, $[M+Na]^+$) 2) ($M = C_{46}H_{32}Cl_4N_{12}O_8$, $[M+k-2H]^+$)

Thus the reaction time of the chlorination was decreased to 5 hours and the elemental analysis of chlorinated product **4** showed that it was a mixture of products with 4- and 3- chlorine atoms at bay region of perylene. (Elemental analysis : Measured: 23.4-23.93%, Calculated: 26.75%). However, it was possible to separate these two products by column chromatography after attaching the azide moiety at the imide position. The elemental analysis of product **5** after purification showed that it contained four chlorine atoms (Measured :20.30% , Calculated: 20.42%). Furthermore the ESI-TOF-MS analysis of the products after the click reaction **1a,b,c** showed that they had been accomplished a clean substitution with four chlorine atoms.

S2- Characterization of compound **5**

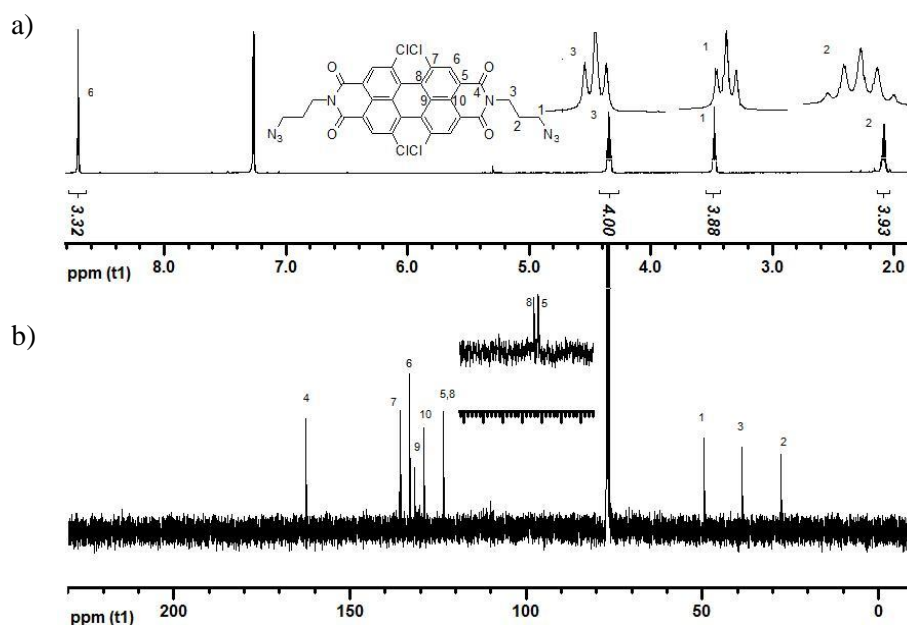


Figure S4. a) ¹H and b) ¹³C NMR spectrum of compound **5** in CDCl₃

S3-Characterization of compound **1a**

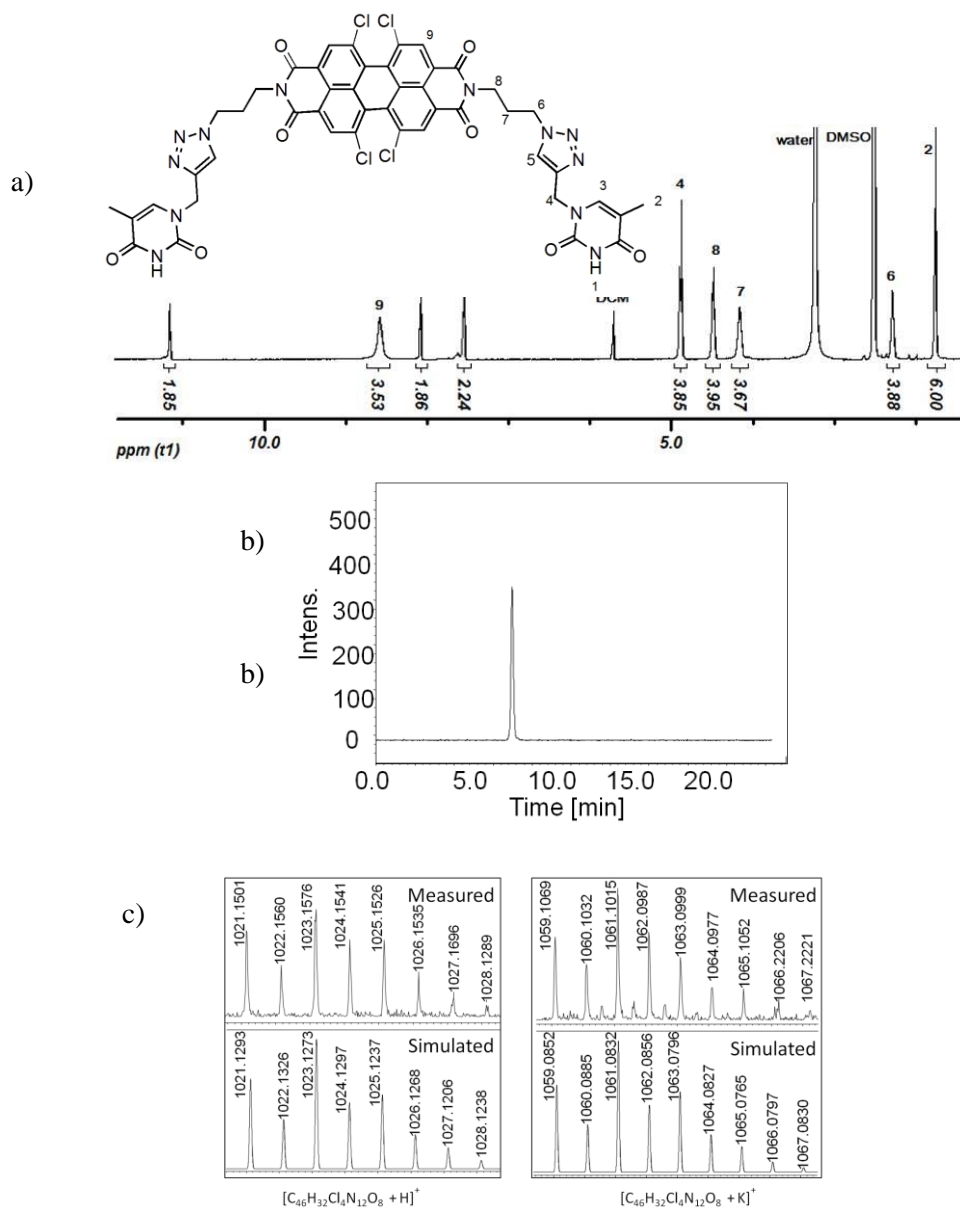
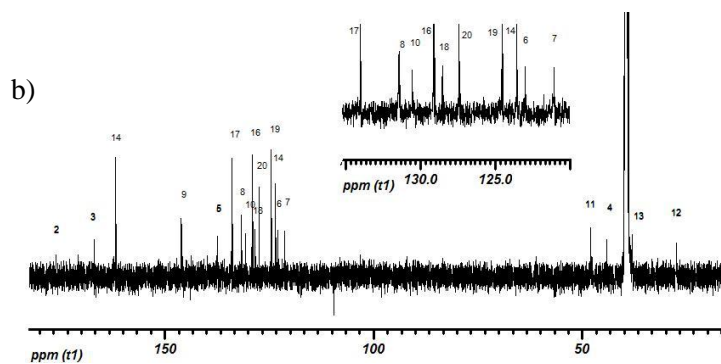
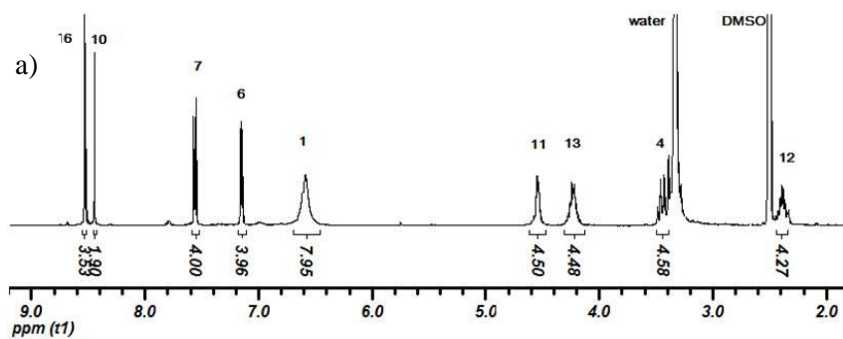
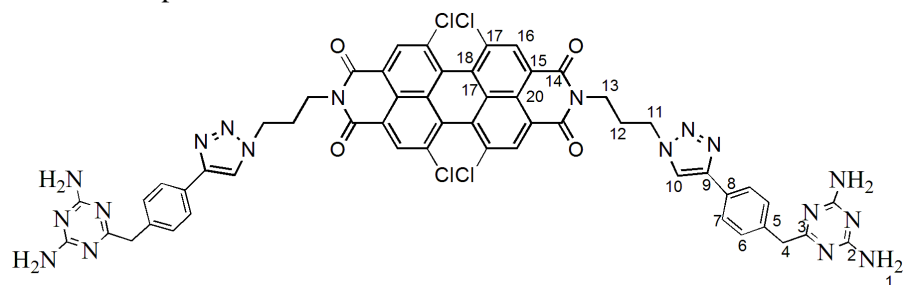


Figure S5. a) ^1H -NMR spectrum in DMSO-d_6 of compound **1a** b) HPLC chromatogram of **1a** at the detecting UV wavelength of 520 nm c) measured (top) and simulated (bottom) isotopic pattern as proton adduct ($M = \text{C}_{46}\text{H}_{32}\text{Cl}_4\text{N}_{12}\text{O}_8$, $[\text{M}+\text{H}]^+$) and potassium adduct ($M = \text{C}_{46}\text{H}_{32}\text{Cl}_4\text{N}_{12}\text{O}_8$, $[\text{M}+\text{K}]^+$)

S4-Characterization of compound **1b**



-The UV chromatogram showed a tailing effect which is related to the hydrogen-bonding interaction of triazine moiety of **1b** with the column material

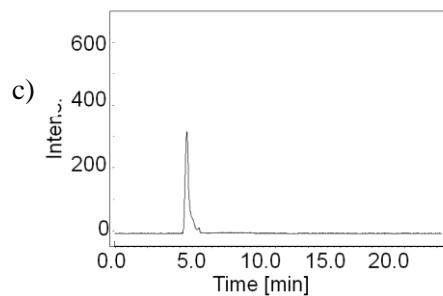


Figure S6. Spectroscopic properties of **1b** a) $^1\text{H-NMR}$ b) $^{13}\text{C-NMR}$ spectrum in DMSO-d_6 c) HPLC chromatogram of **1b** at the detecting UV wavelength of 520 nm

S5-Characterization of compound 1c

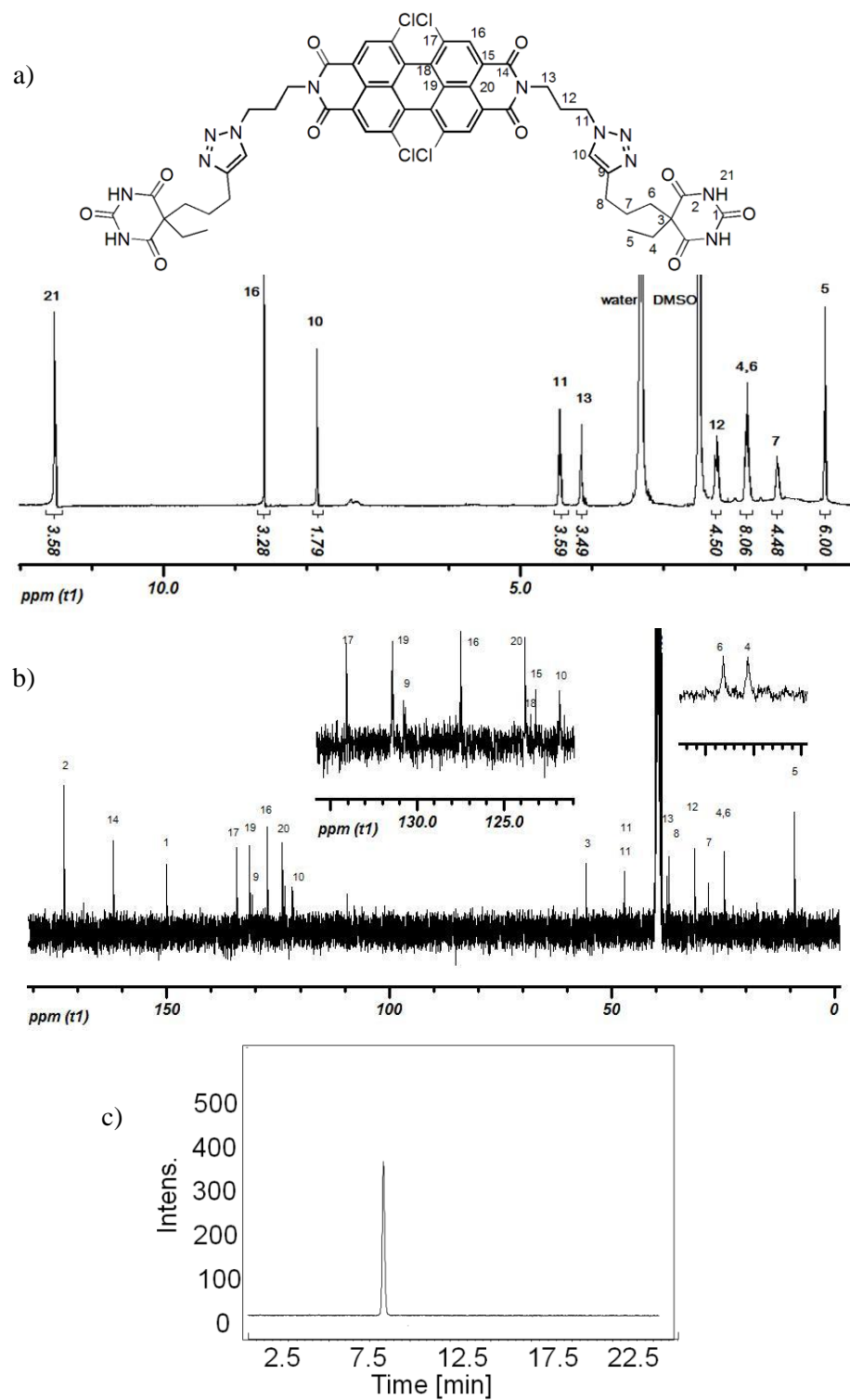


Figure S7. Spectroscopic properties of **1c** a) $^1\text{H-NMR}$ b) $^{13}\text{C-NMR}$ in DMSO-d_6 c) HPLC chromatogram of **1c** at the detecting UV wavelength of 520 nm

S6-Characterization of compound 2a

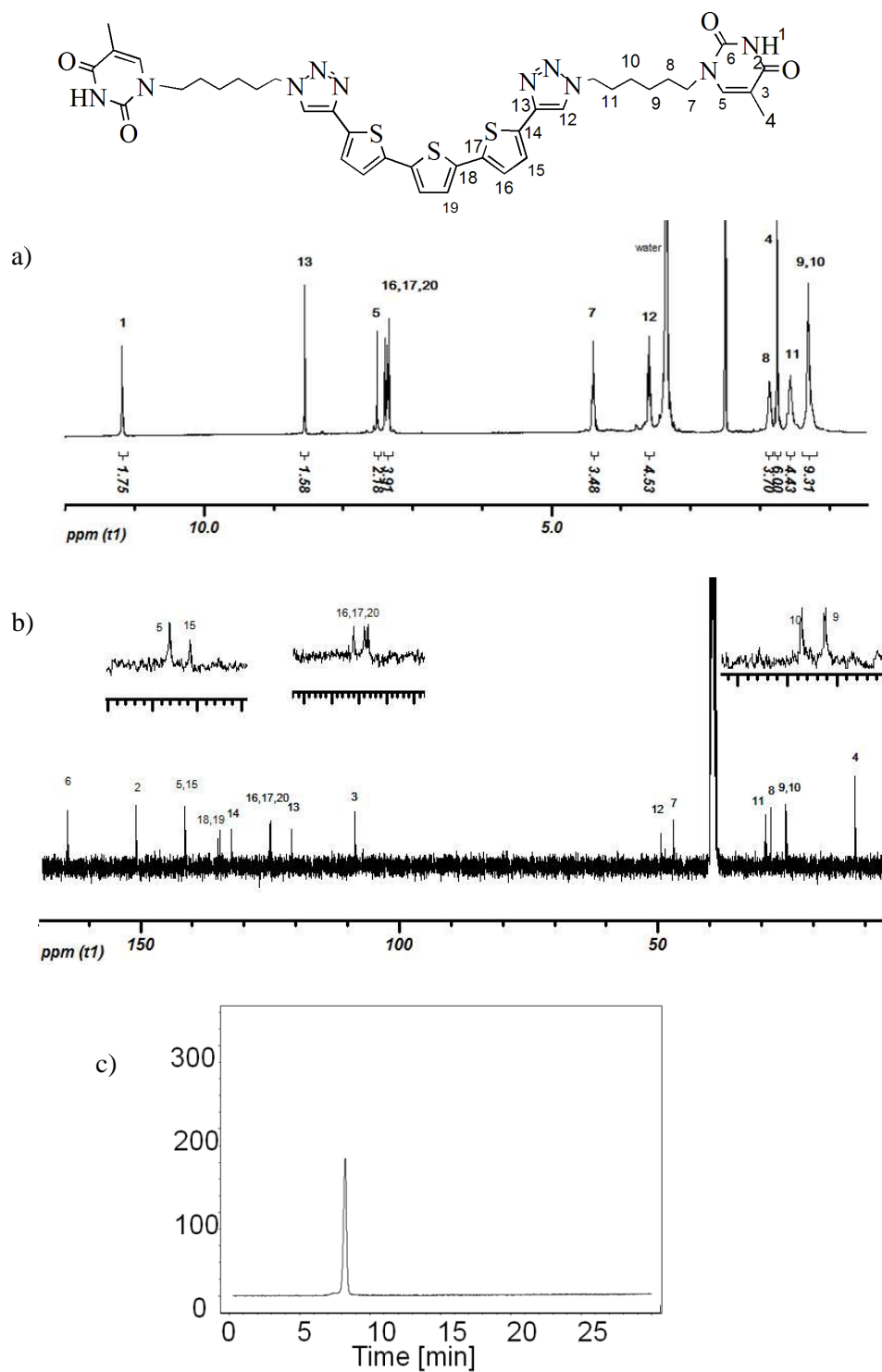


Figure S8. Spectroscopic properties of **2a** a) $^1\text{H-NMR}$ b) $^{13}\text{C-NMR}$ in DMSO-d_6 c) HPLC chromatogram of **2a** at the detecting UV wavelength of 400 nm

S7-Characterization of compound **2b**

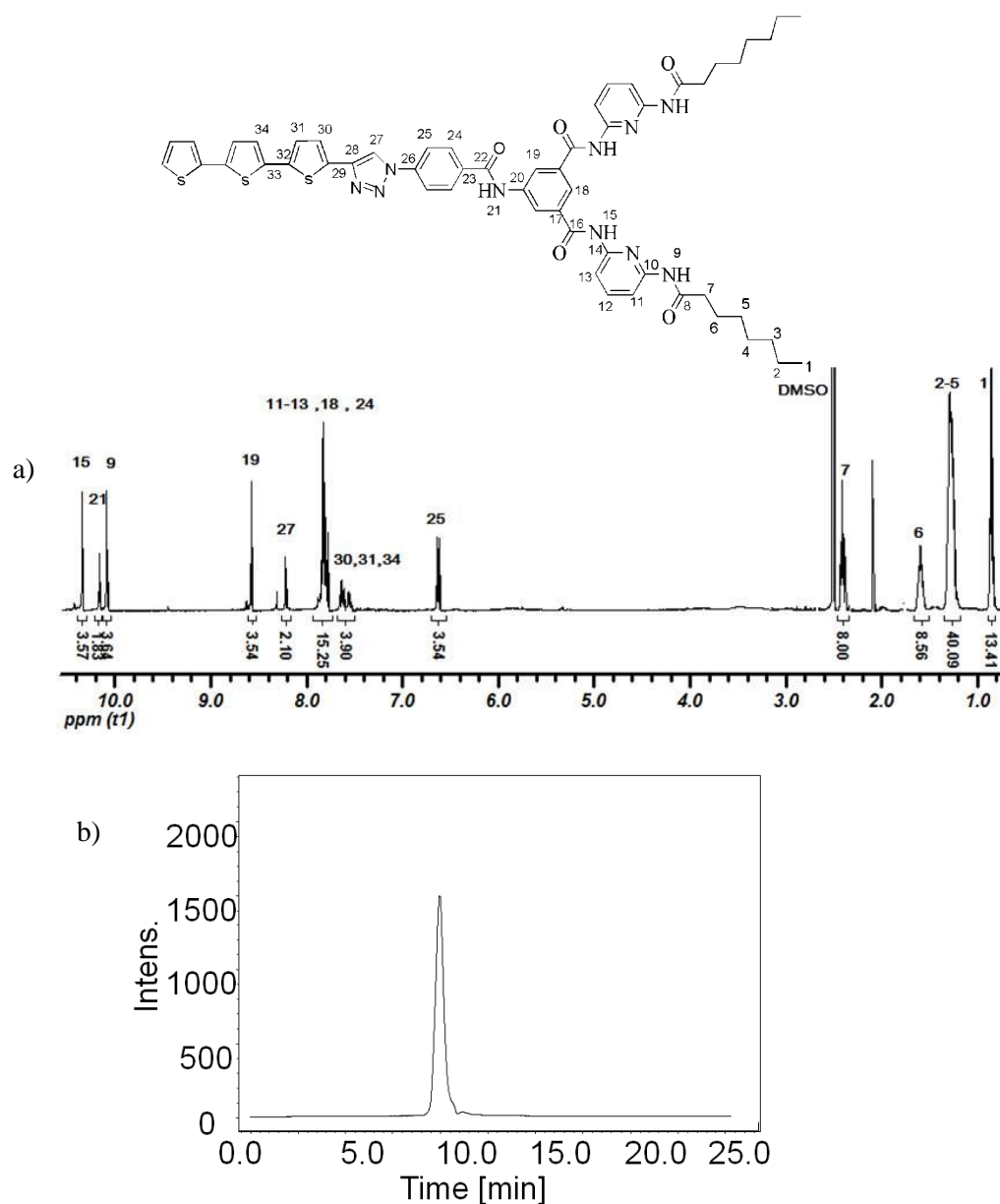


Figure S9. a) ¹H-NMR spectrum of **2b** in DMSO-d₆ b) HPLC chromatogram of **2b** at detecting UV wavelength of 300 nm

(1) Baggerman, J.; Jagesar, D. C.; Vallée, R. A. L.; Hofkens, J.; De Schryver, F. C.; Schelhase, F.; Vögtle, F.; Brouwer, A. M. *Chem. Eur. J.* **2007**, *13*, 1291-1299.