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Supporting Information

Ultrabright Red-Emitting Photostable Perylene Bisimide Dyes: New Indicators for Ratiometric Sensing of High pH or Carbon Dioxide

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Supporting Information

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pH Sensing Properties

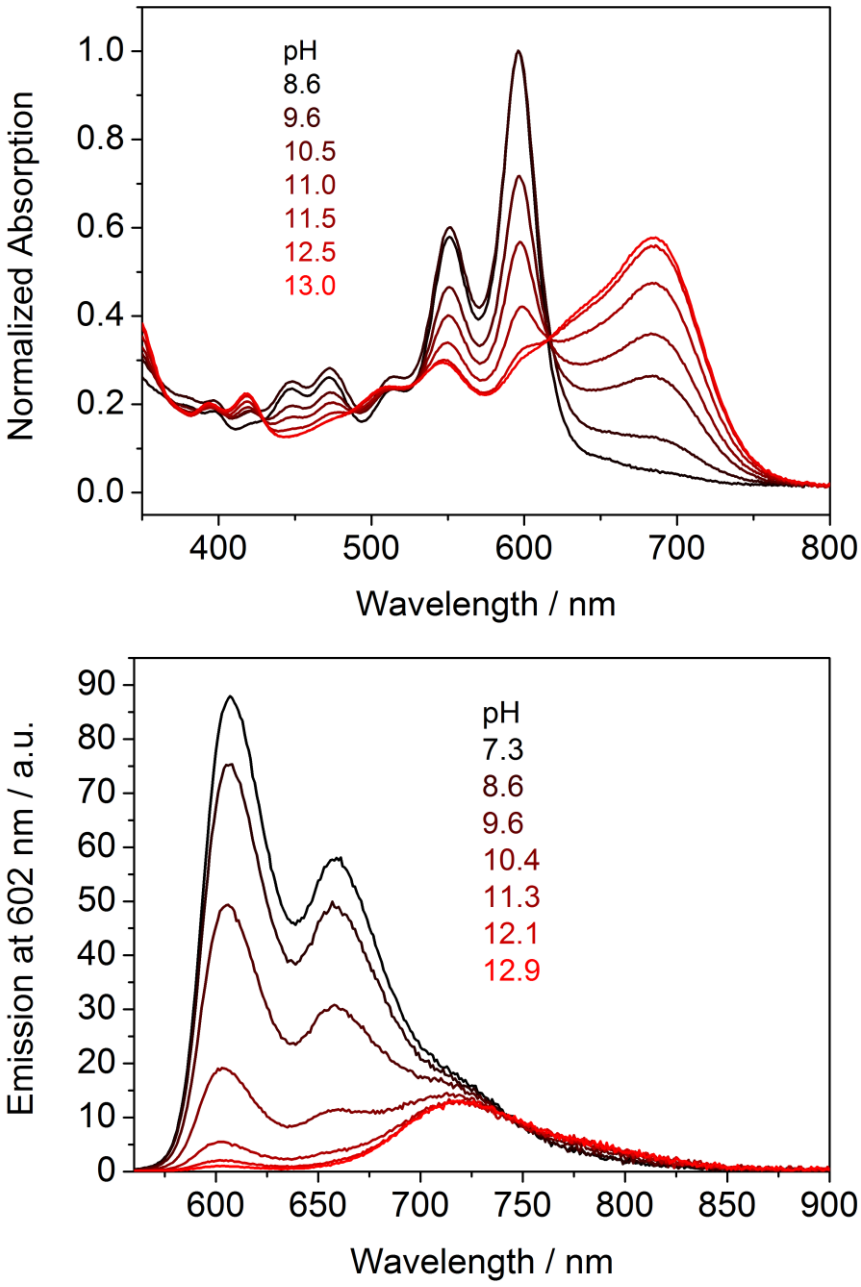

Figure S1. pH dependence of absorption and fluorescence spectra of **2b** embedded in hydrogel D4, measured at 25°C (λ_{exc} 528 nm).

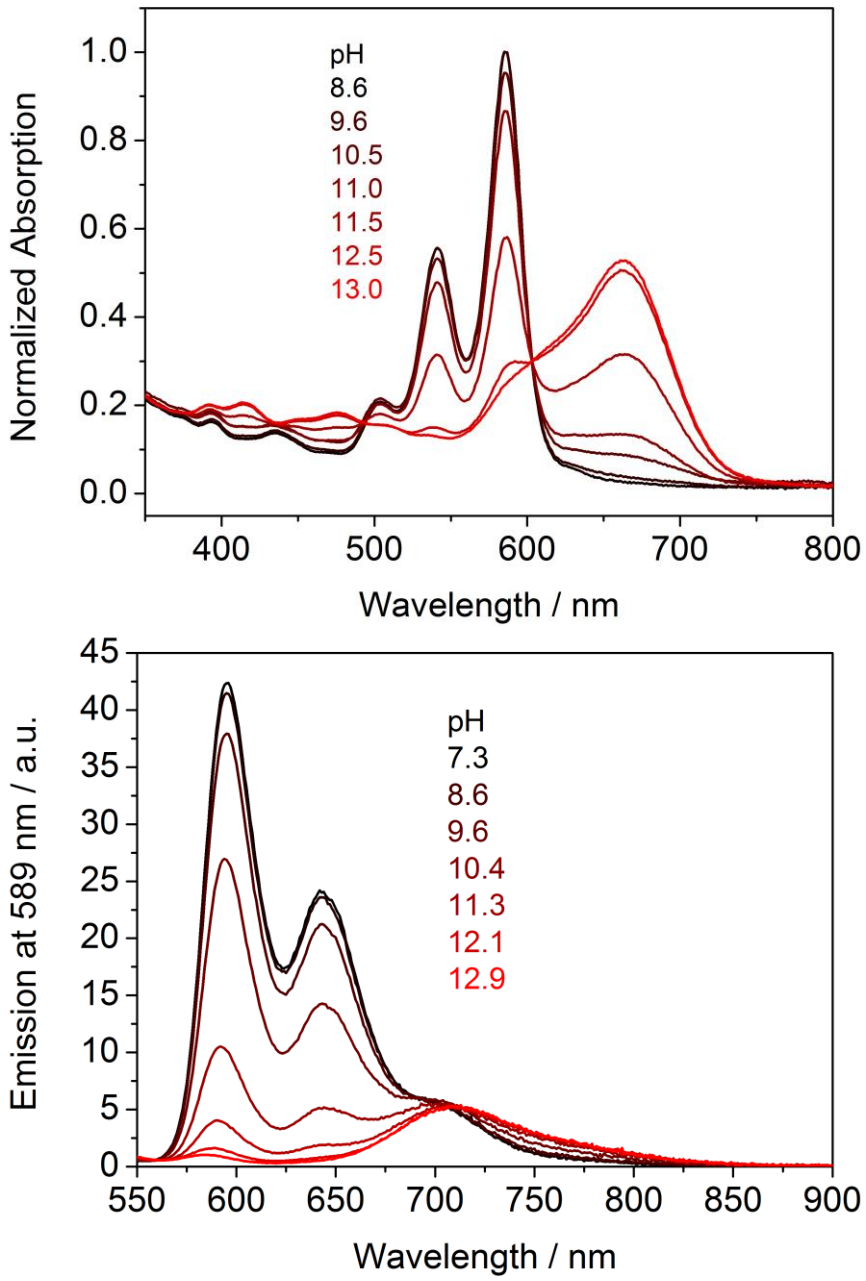

Figure S2. pH dependence of absorption and fluorescence spectra of **2c** embedded in hydrogel D4, measured at 25°C (λ_{exc} 493 nm).

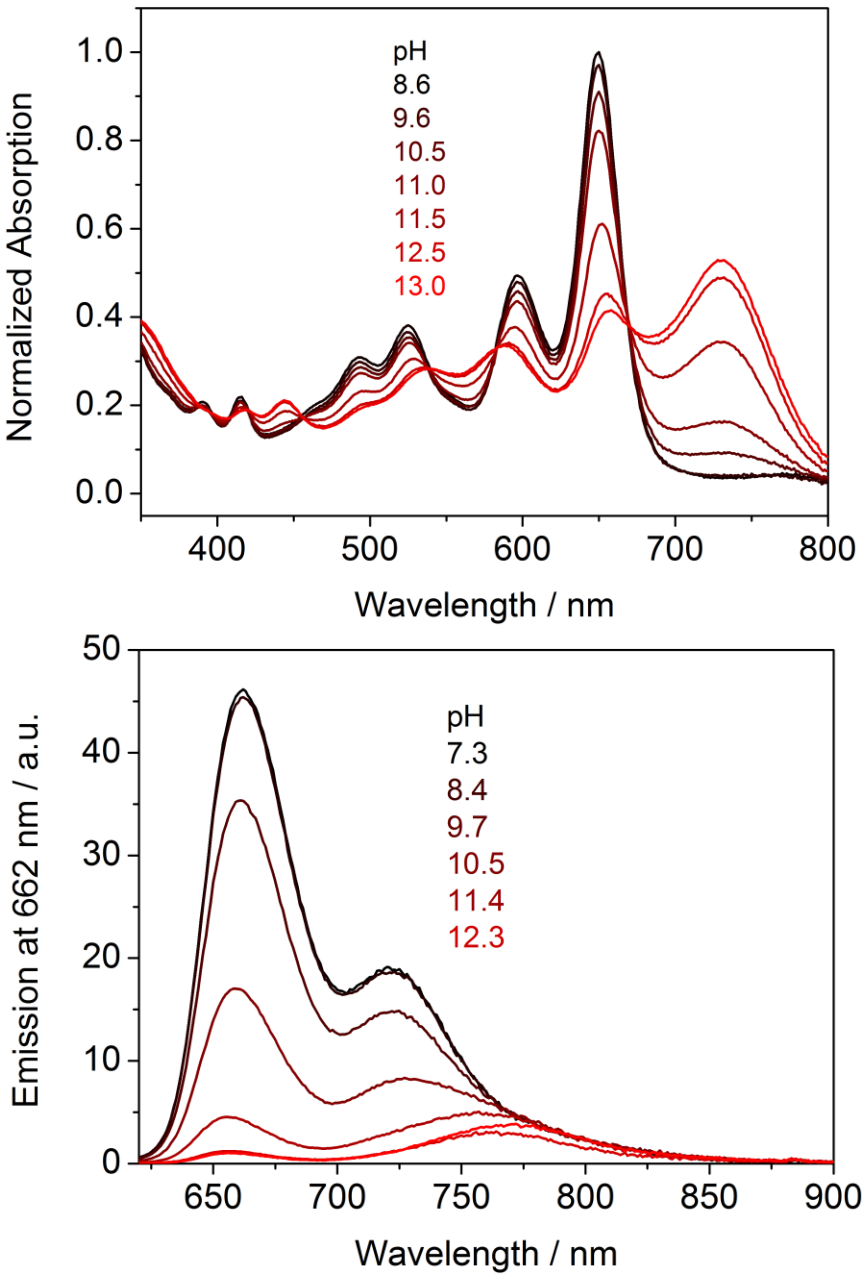

Figure S3. pH dependence of absorption and fluorescence spectra of **3a** embedded in hydrogel D4, measured at 25°C (λ_{exc} 590 nm).

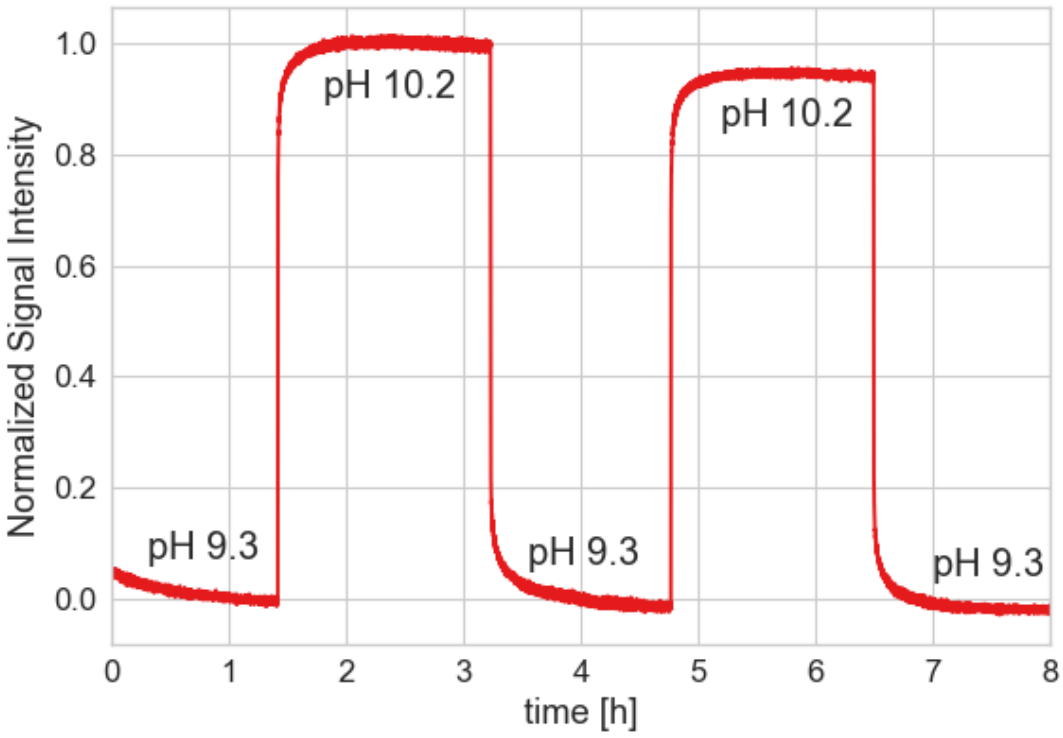

Figure S4. Reversible sensor response to dynamic pH changes measured in buffer solutions at 25°C.

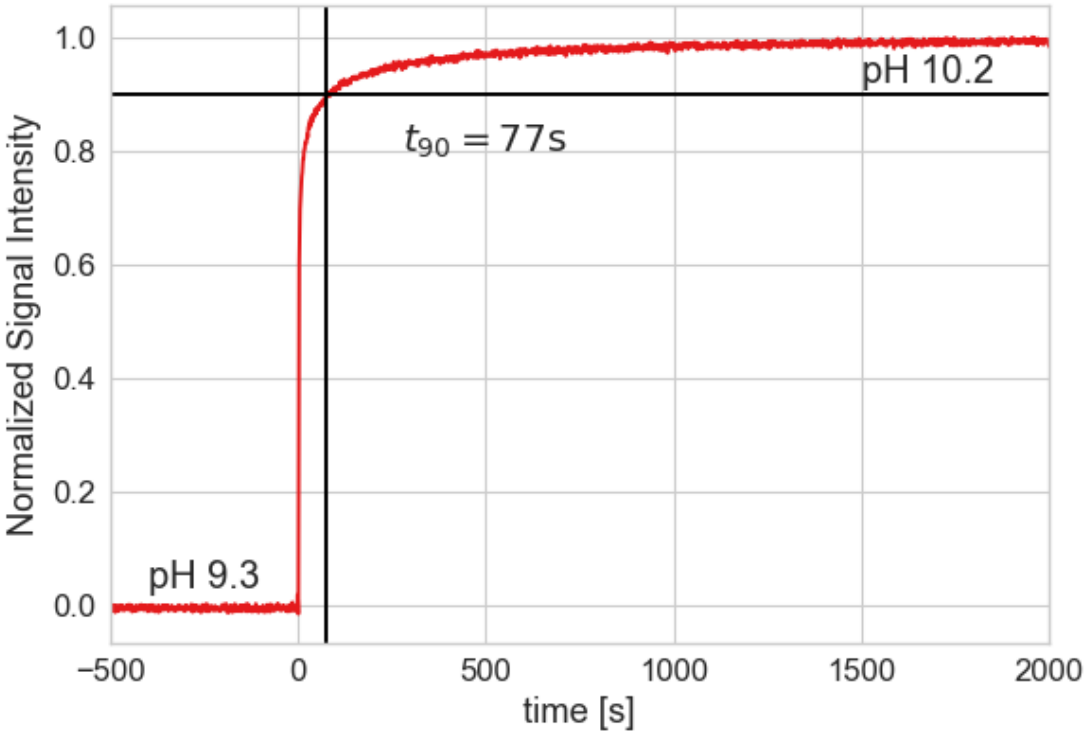

Figure S5. Measurement of t_{90} response time from pH 9.3-10.2 at 25°C.

CO_2 Sensing Properties

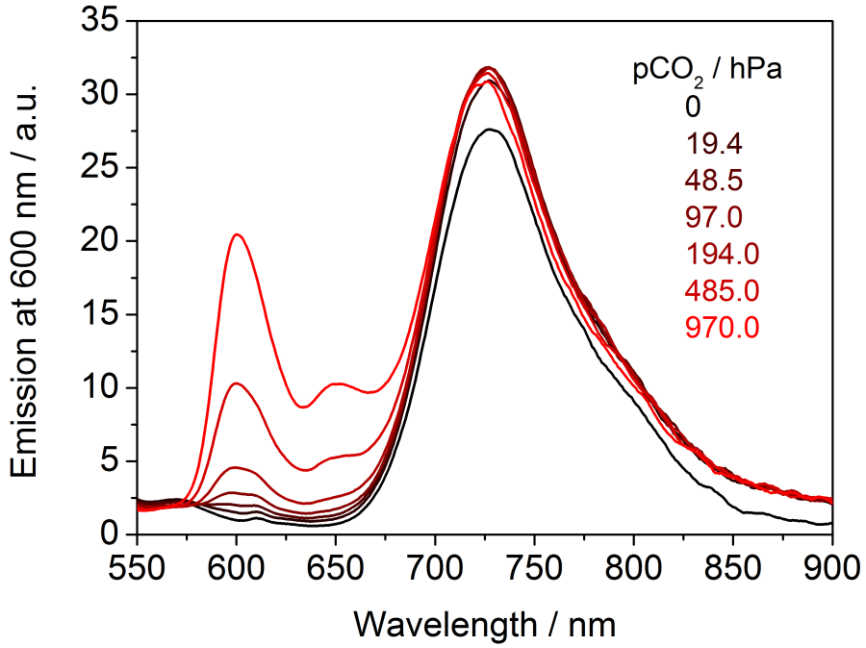

Figure S6. Fluorescence spectra of CO2_1 sensor foil measured in water at different pCO_2 (25°C).

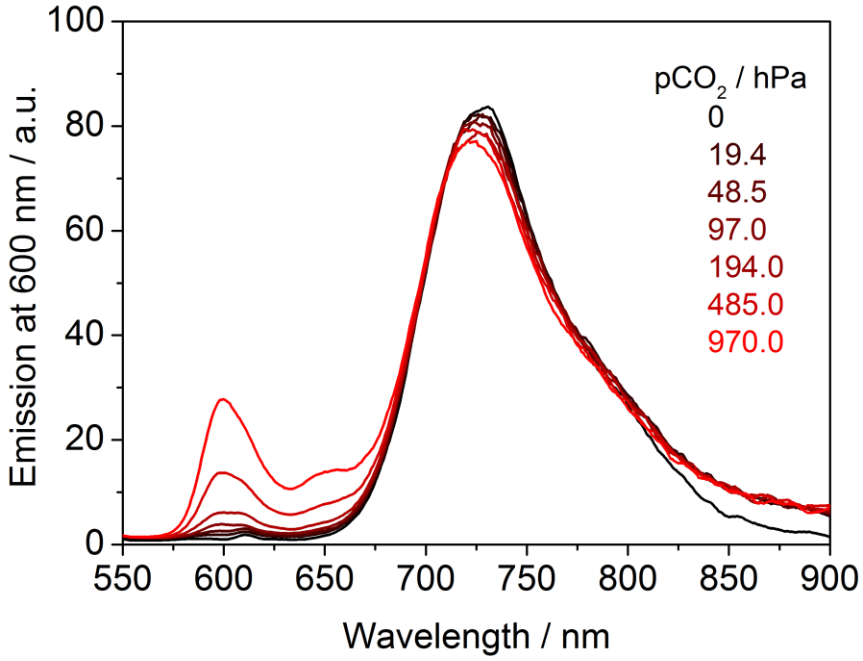

Figure S7. Fluorescence spectra of CO2_2 sensor foil measured in water at different pCO_2 (25°C).

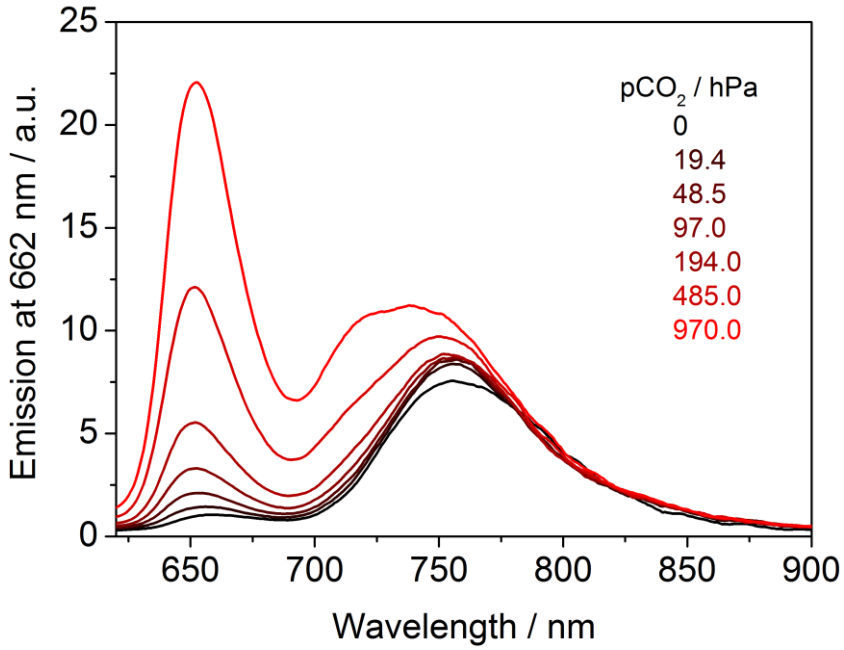

Figure S8. Fluorescence spectra of CO2_8 sensor foil measured in water at different pCO_2 (25°C).

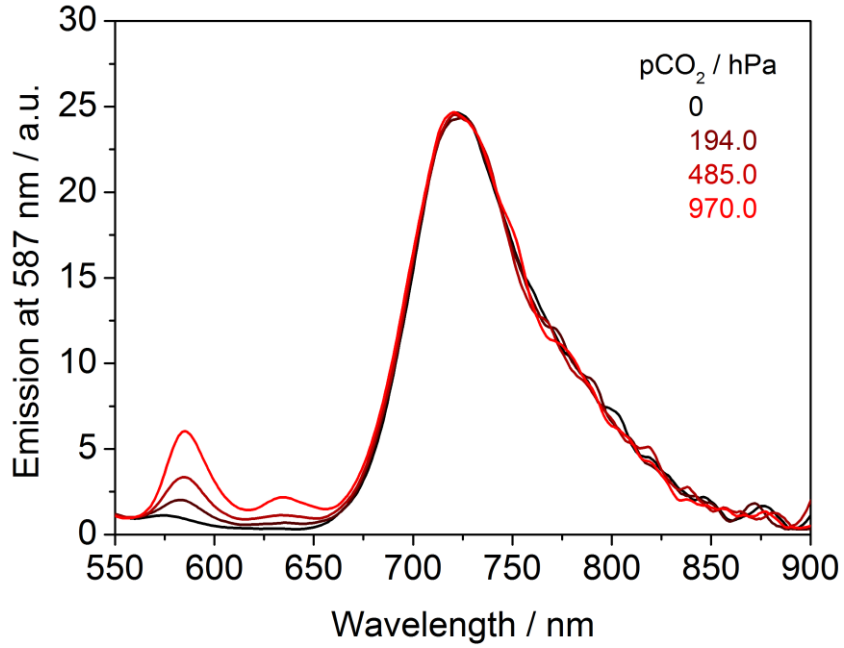

Figure S9. Fluorescence spectra of CO2_4 sensor foil measured in water at different pCO_2 (25°C).

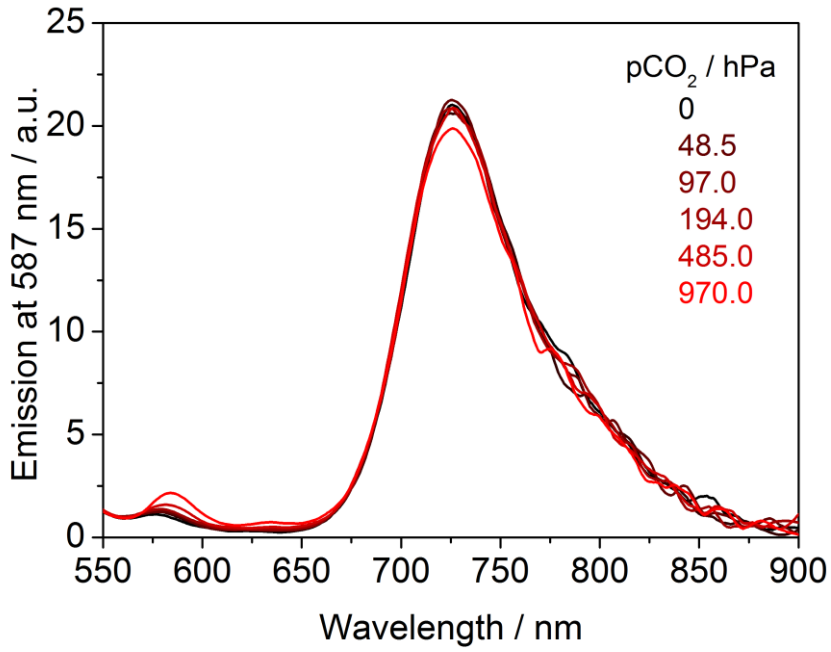

Figure S10. Fluorescence spectra of CO2_5 sensor foil measured in water at different pCO_2 (25°C).

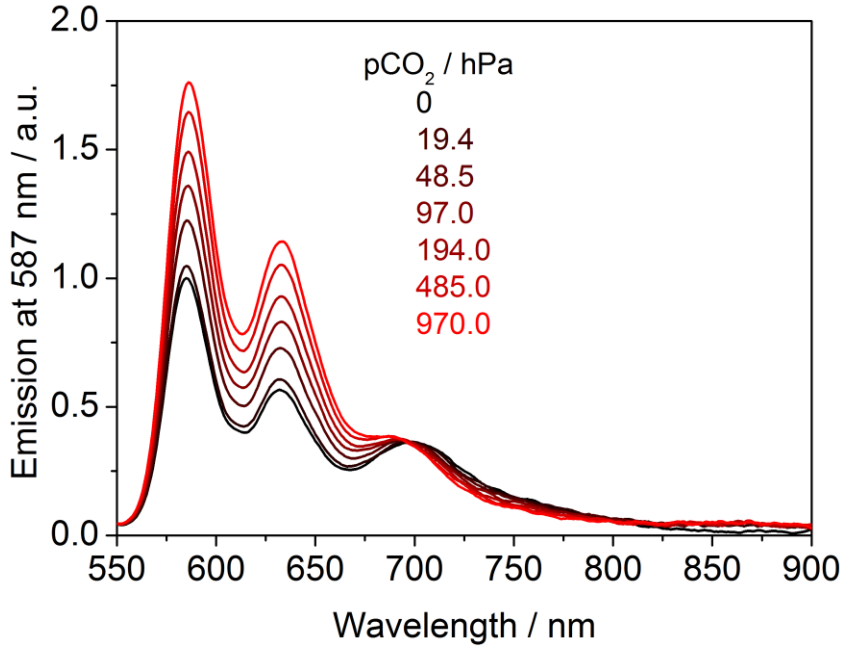

Figure S11. Fluorescence spectra of CO2_6 sensor foil measured in water at different pCO_2 (25°C).

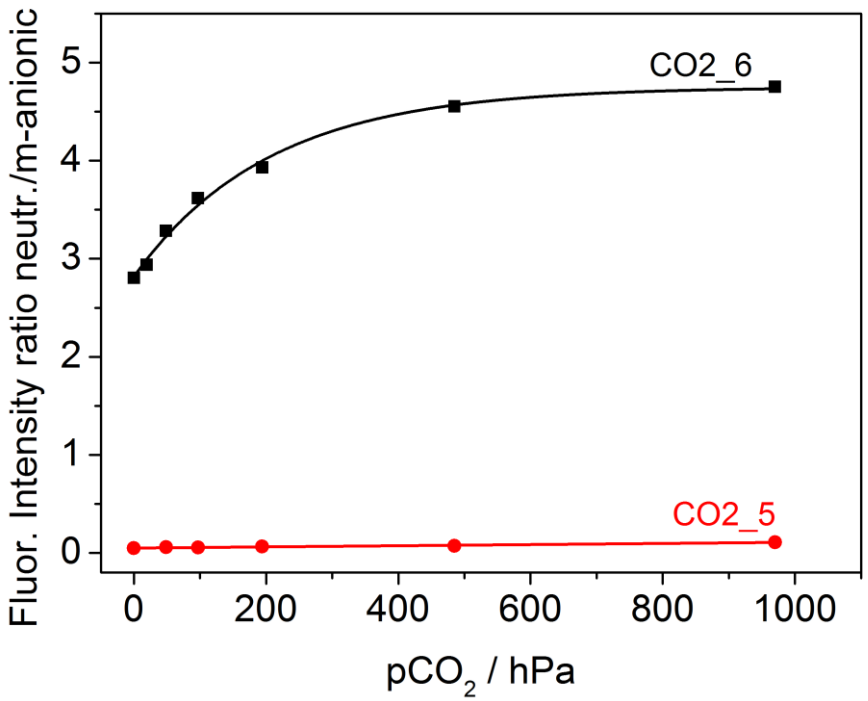

Figure S12. Corresponding calibration curves of CO2_5 and CO2_6.

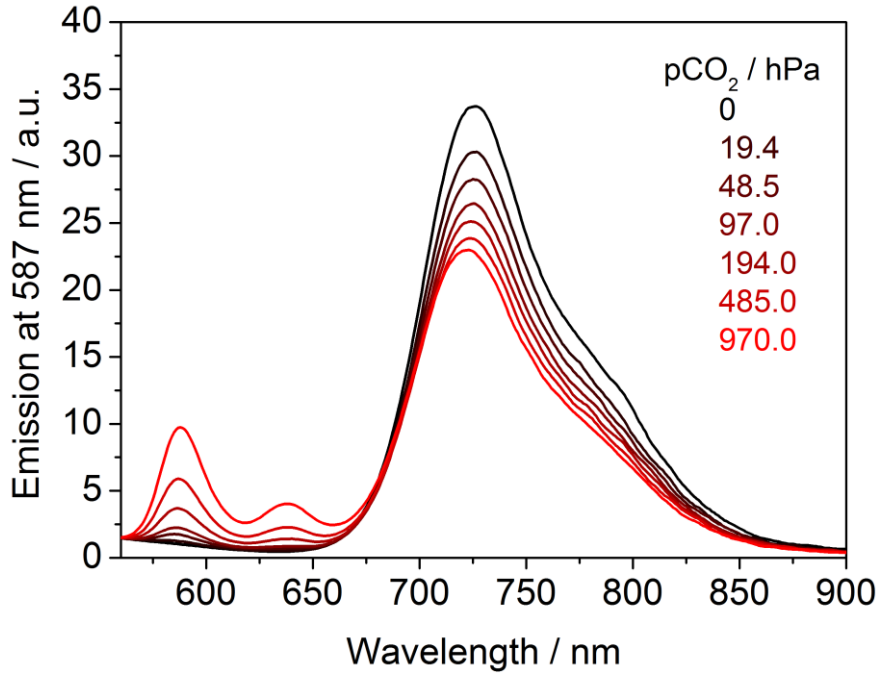

Figure S13. Fluorescence spectra of CO2_3 sensor foil measured in gas phase at 85% relative humidity at different pCO_2, regulated by bubbling CO_2 through saturated KCl solution (25°C).

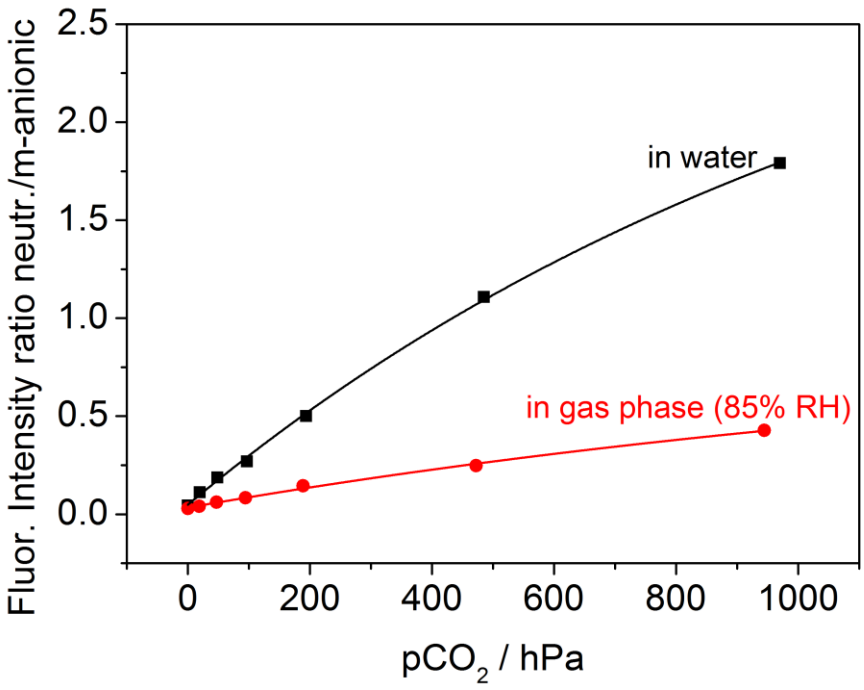

Figure S14. Corresponding calibration curves of CO2_3 sensor foil calibrated in water and in gas phase at 85% relative humidity.

NMR Spectra

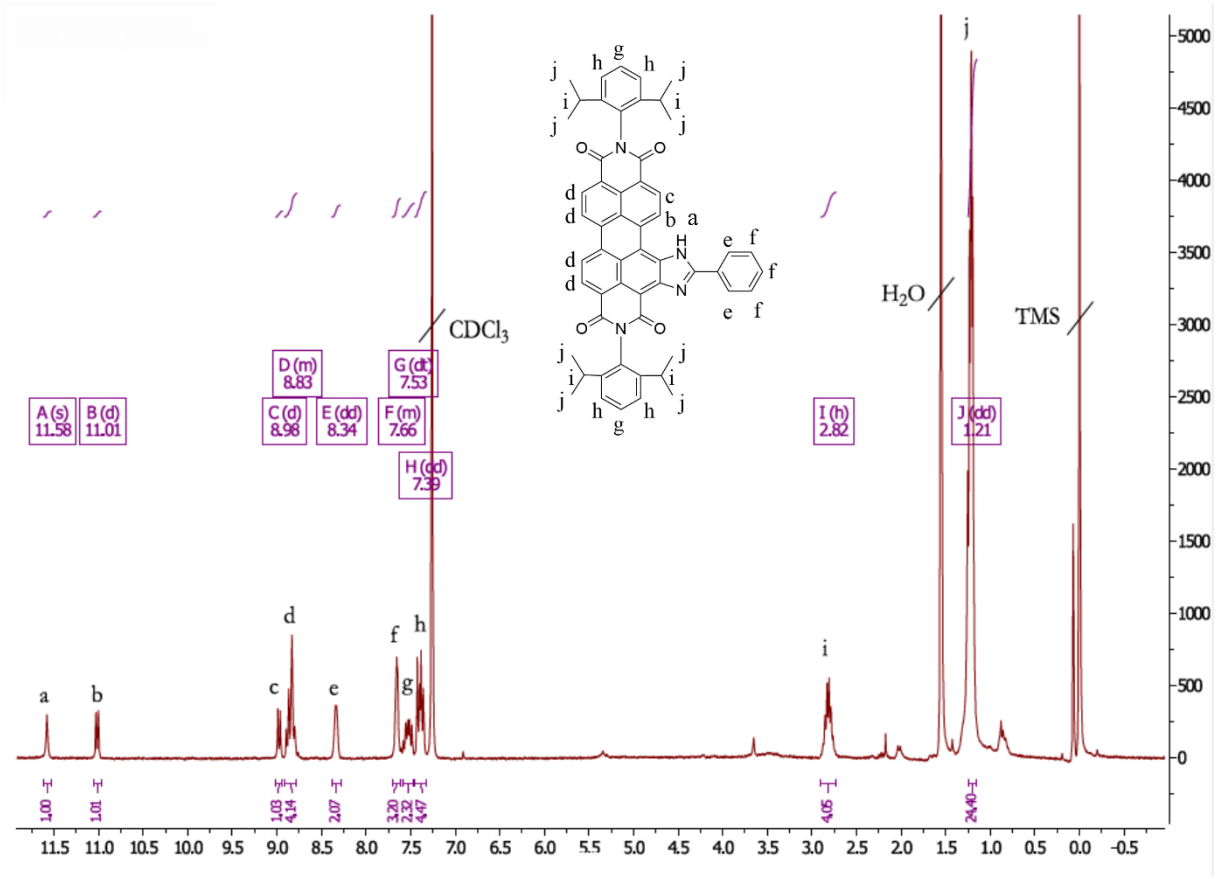

Figure S15. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2a**.

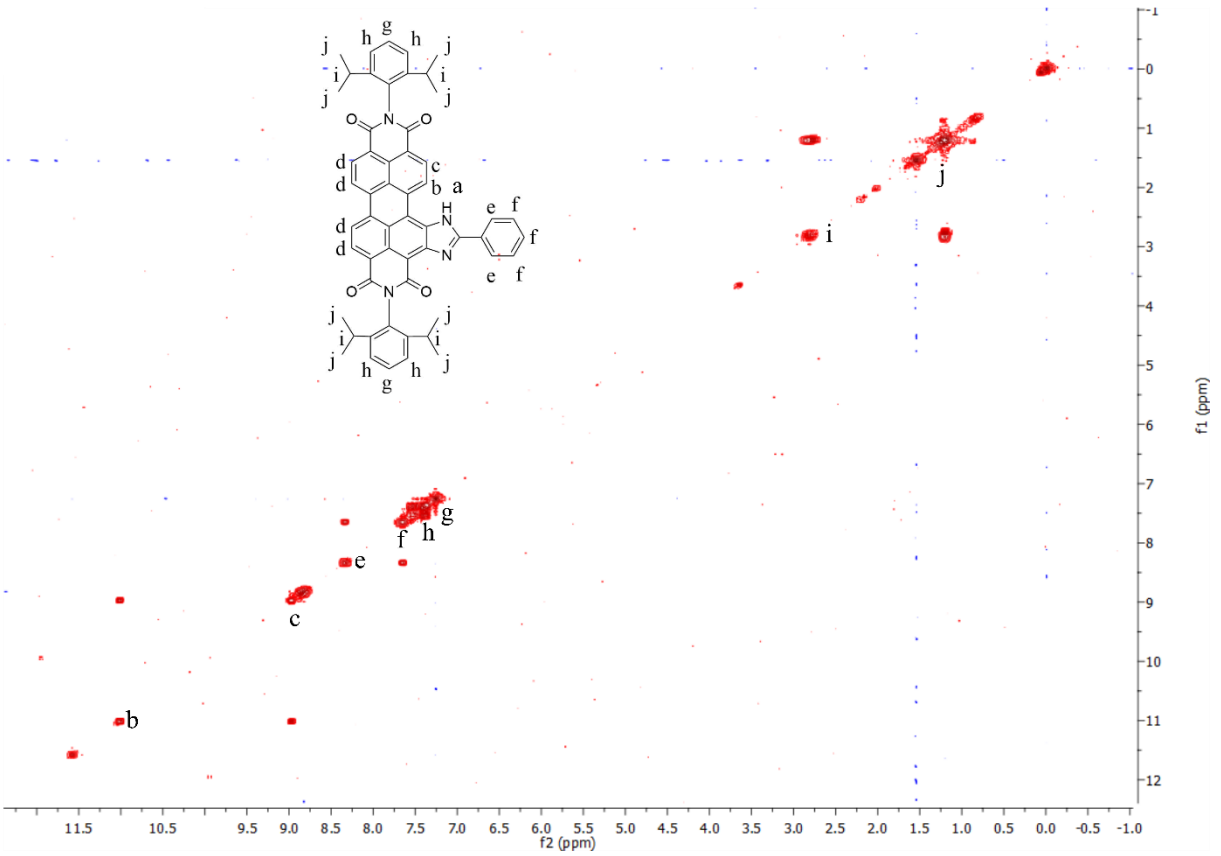

Figure S16. Cosy NMR ($CDCl_3$, 300 MHz) of **2a**.

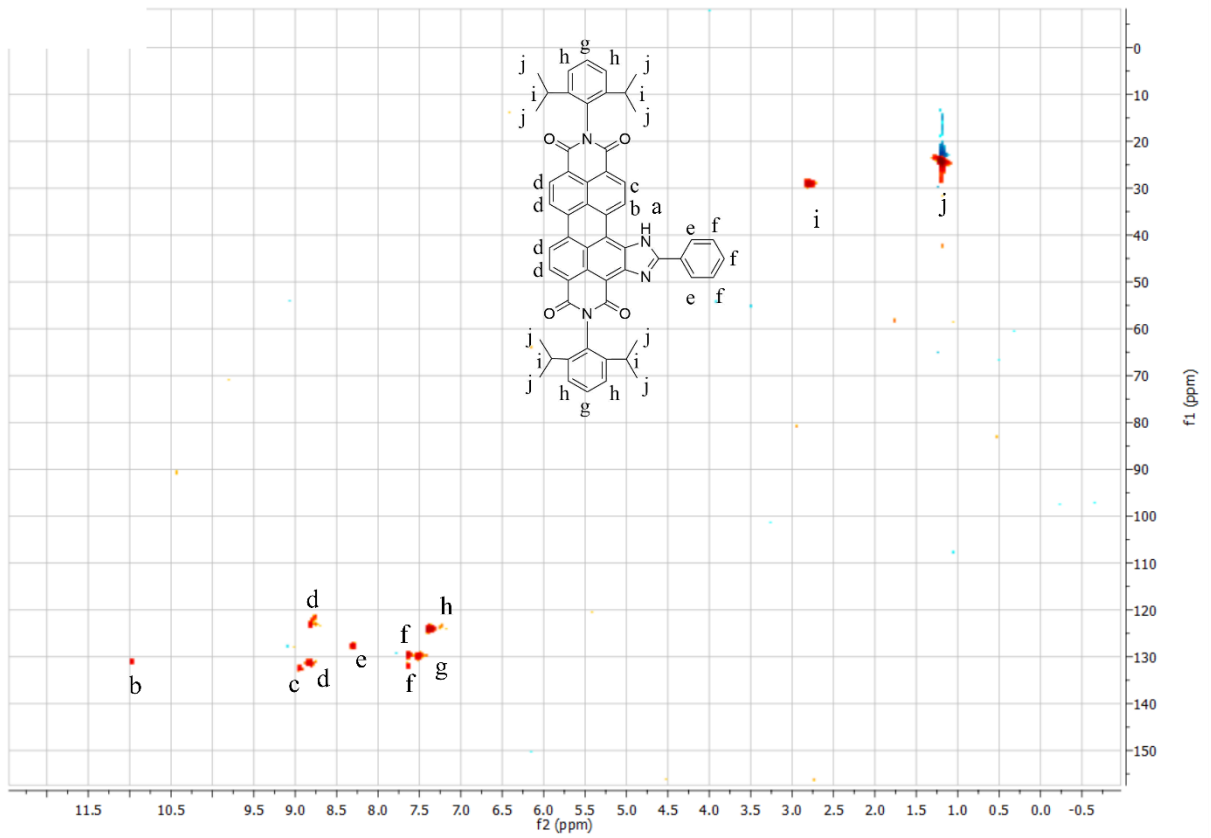

Figure S17. HSQC NMR ($CDCl_3$, 500 MHz, 126 MHz) of **2a**.

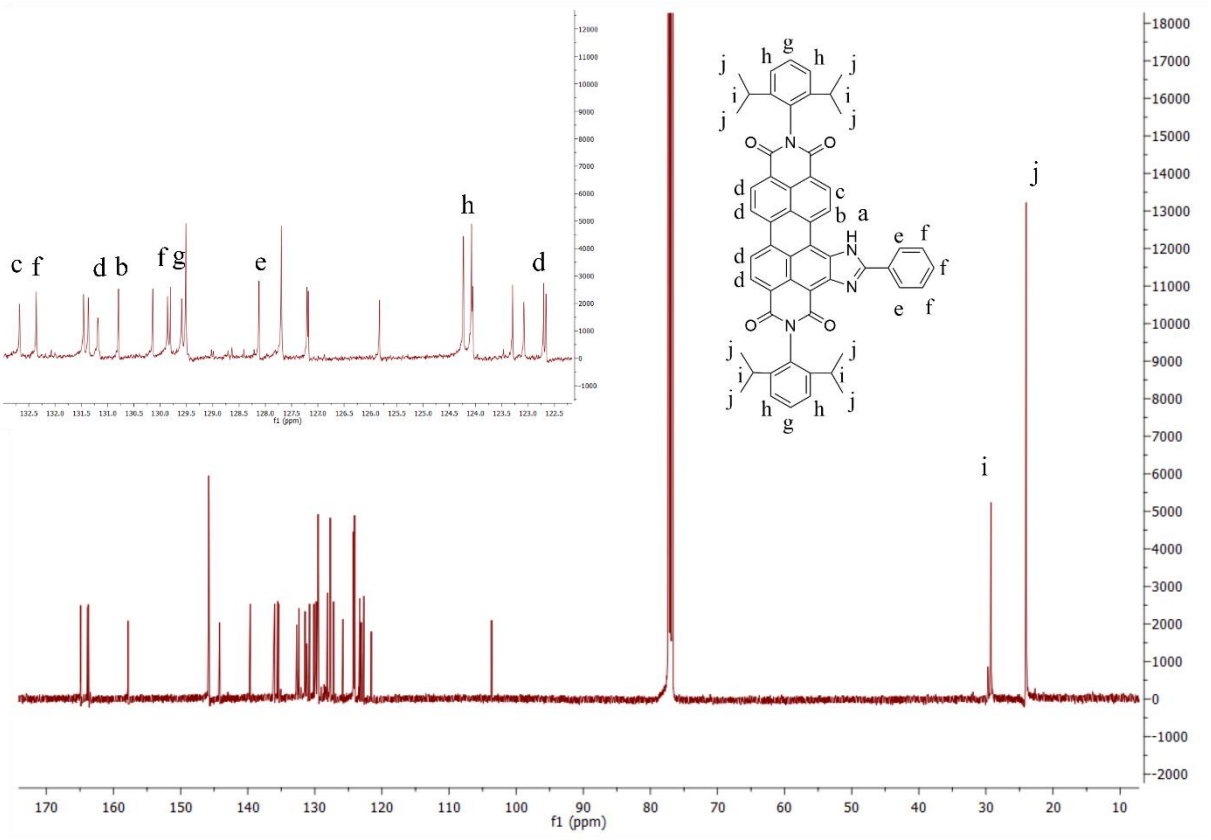

Figure S18. ^{13}C NMR ($CDCl_3$, 126 MHz) of **2a**.

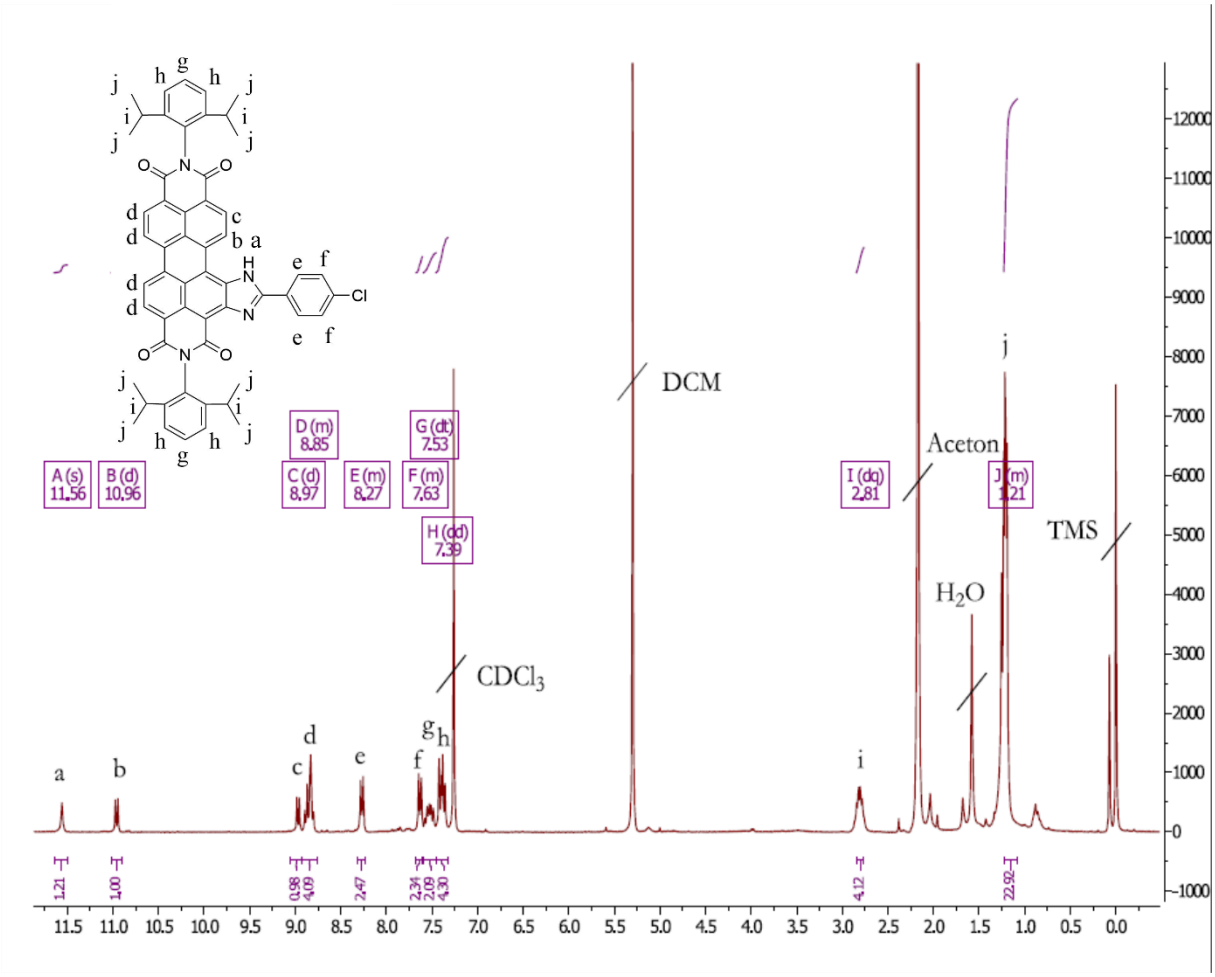

Figure S19. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2b**.

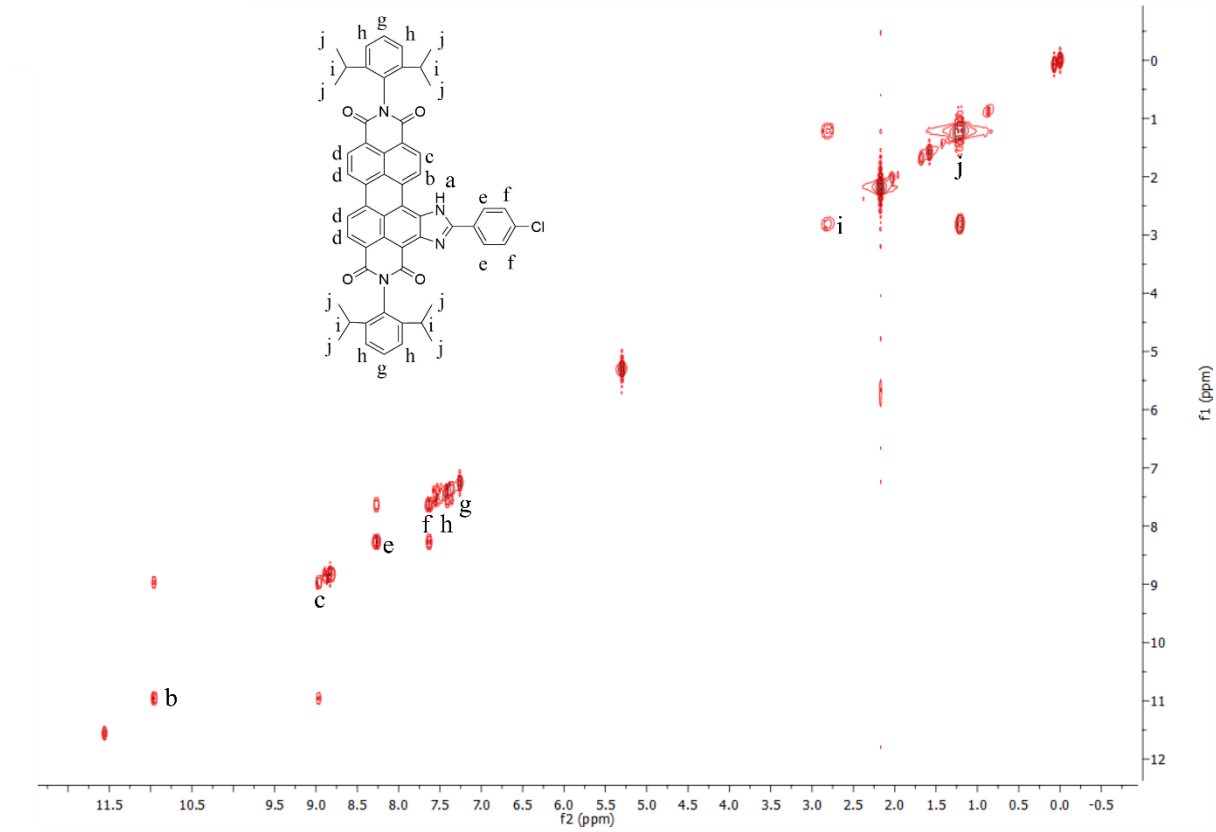

Figure S20. Cosy NMR ($CDCl_3$, 300 MHz) of **2b**.

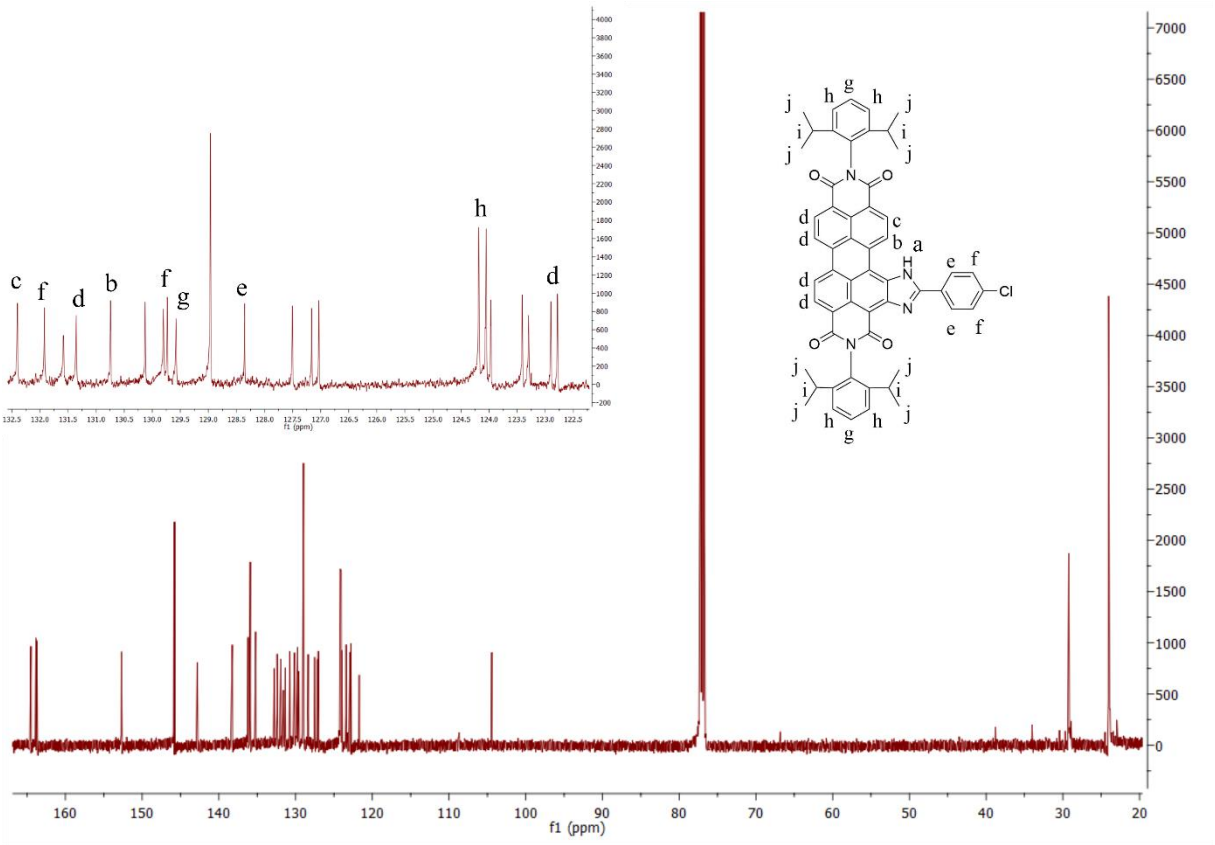

Figure S21. ^{13}C NMR ($CDCl_3$, 126 MHz) of **2b**.

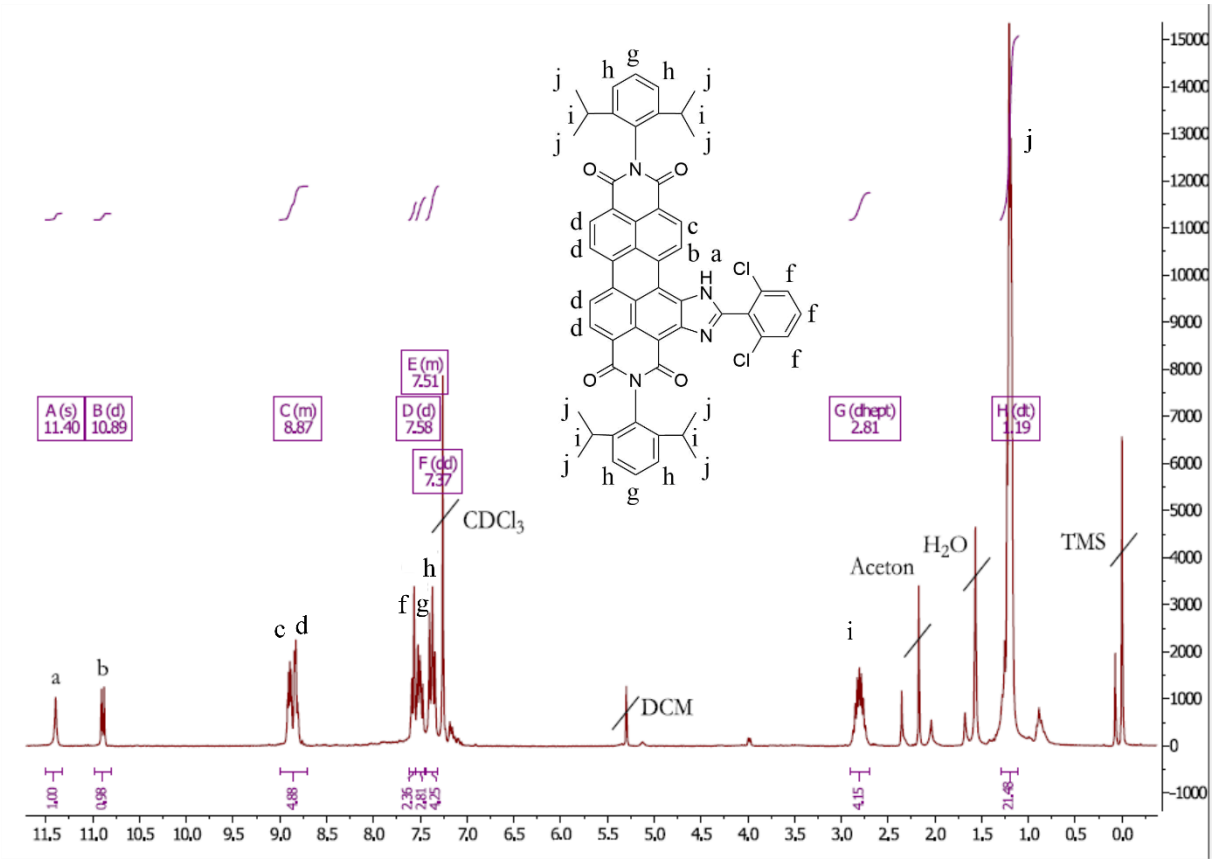

Figure S22. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2c**.

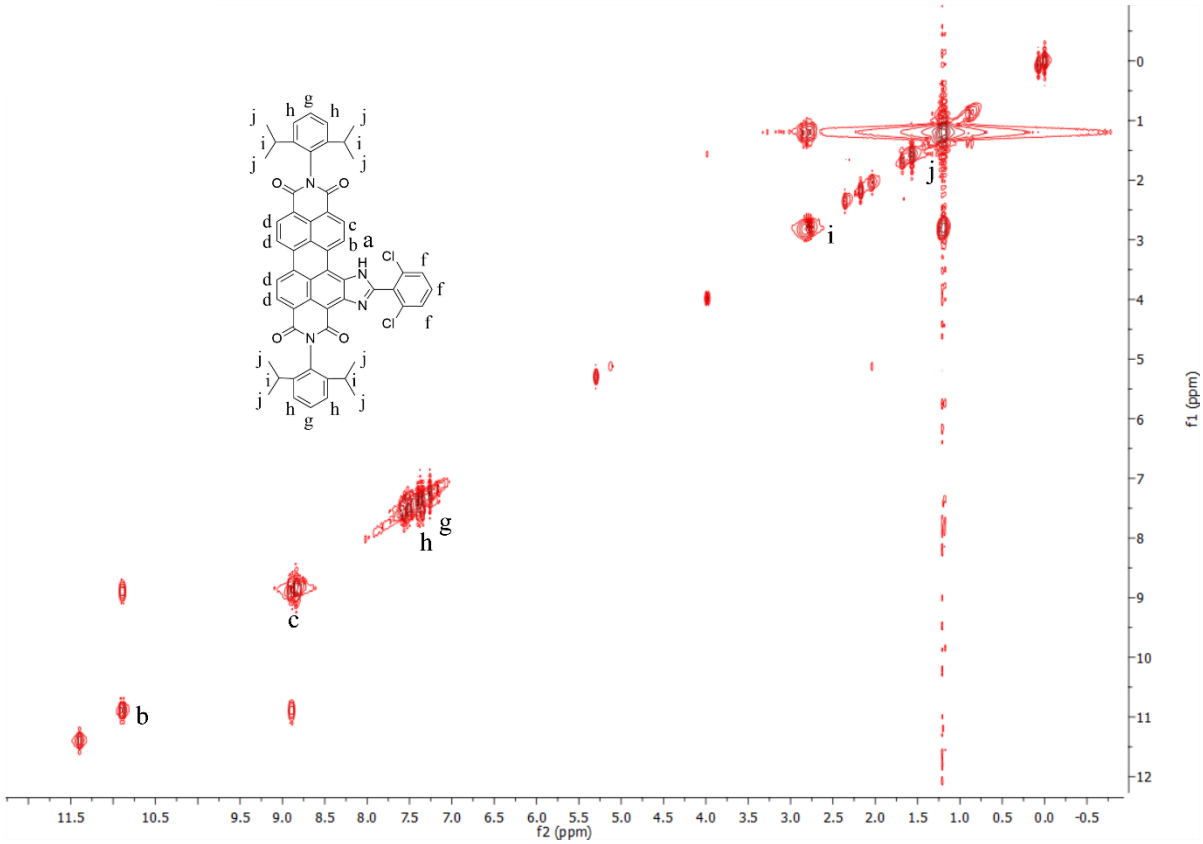

Figure S23. Cosy NMR ($CDCl_3$, 300 MHz) of **2c**.

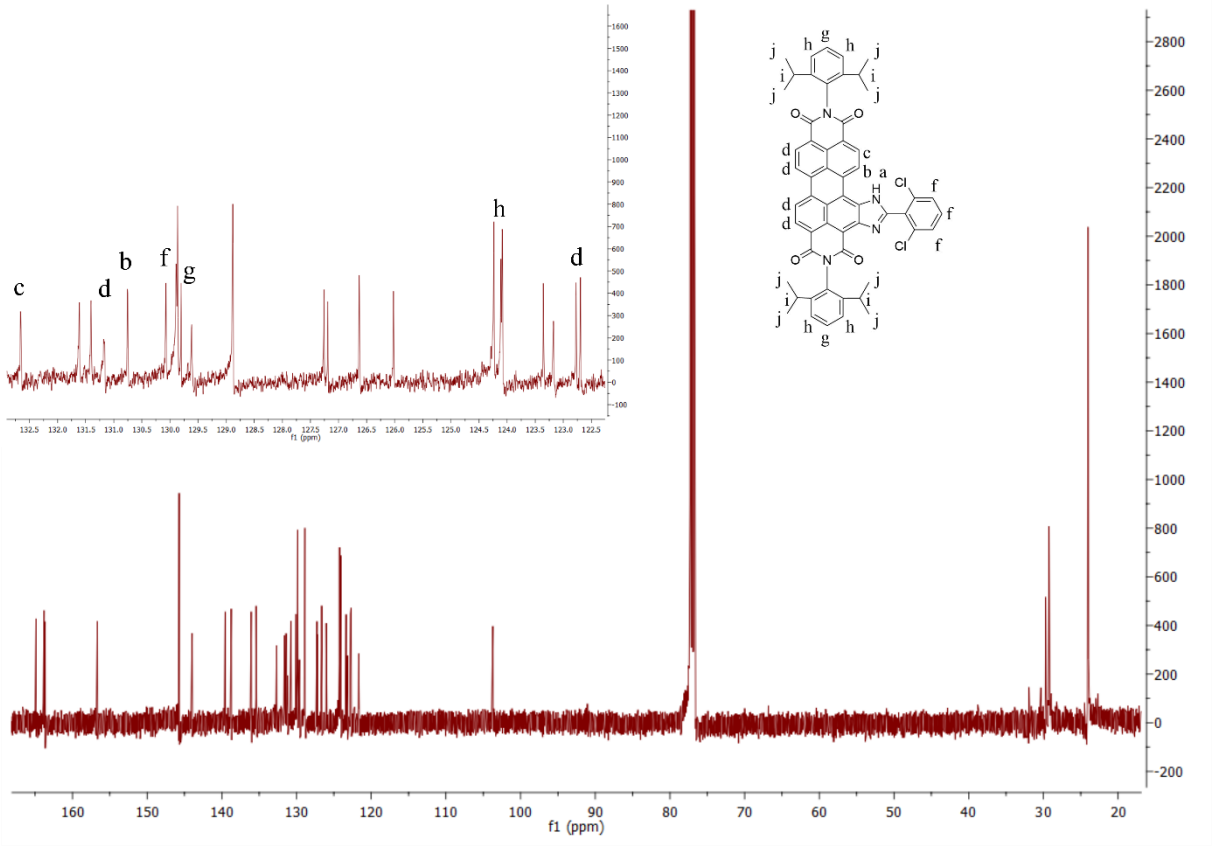

Figure S24. ^{13}C NMR ($CDCl_3$, 126 MHz) of **2c**.

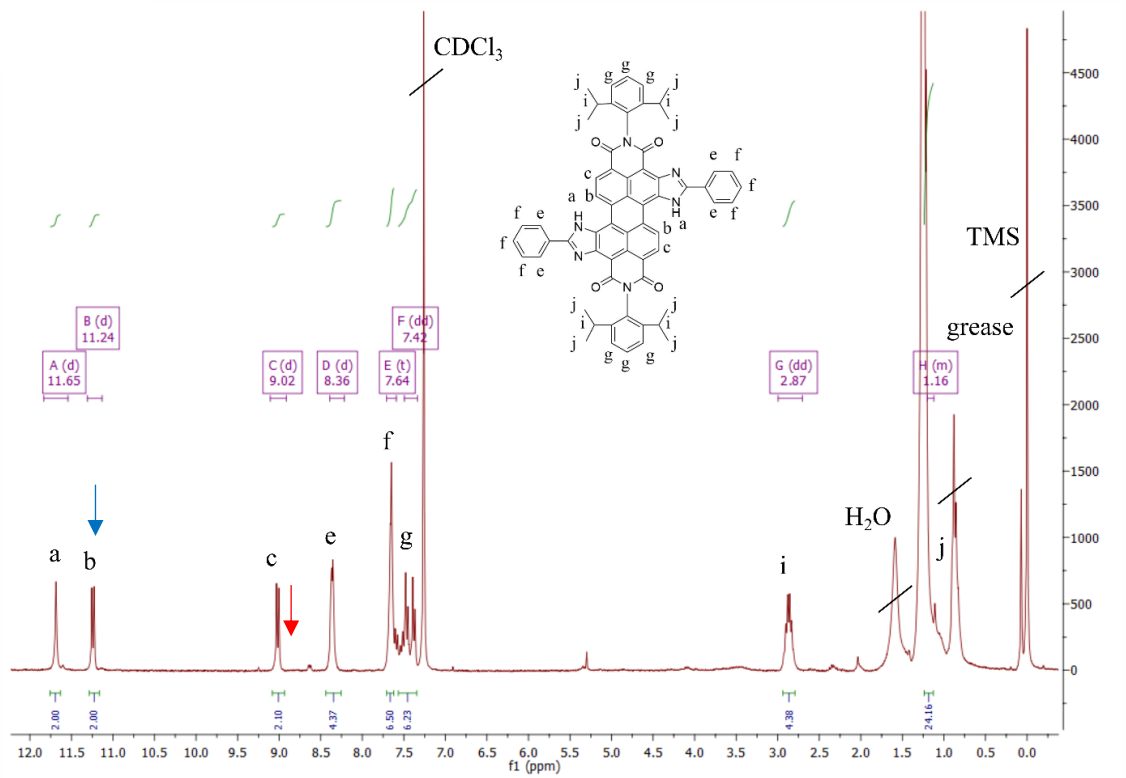

Figure S25. ^{1}H NMR ($CDCl_3$, 300 MHz) of **3a.** The red arrow indicates the signals at around 8.85 ppm which would be expected for the H-atoms located on the opposite side of the perylene for the regioisomer bearing both phenyl-imidazol groups only on one side of the perylene (compare to the signals of *d*-protons in ^{1}H NMR of **2a**, **2b** and **2c** (Fig. S15, S19, S22)). Additionally, the signal from the protons *b* (blue arrow) is located at about 11 ppm (similarly to the protons in **2a**, **2b** and **2c)** which is due to the proximity NH group. The regioisomer would not show protons with such a shift.

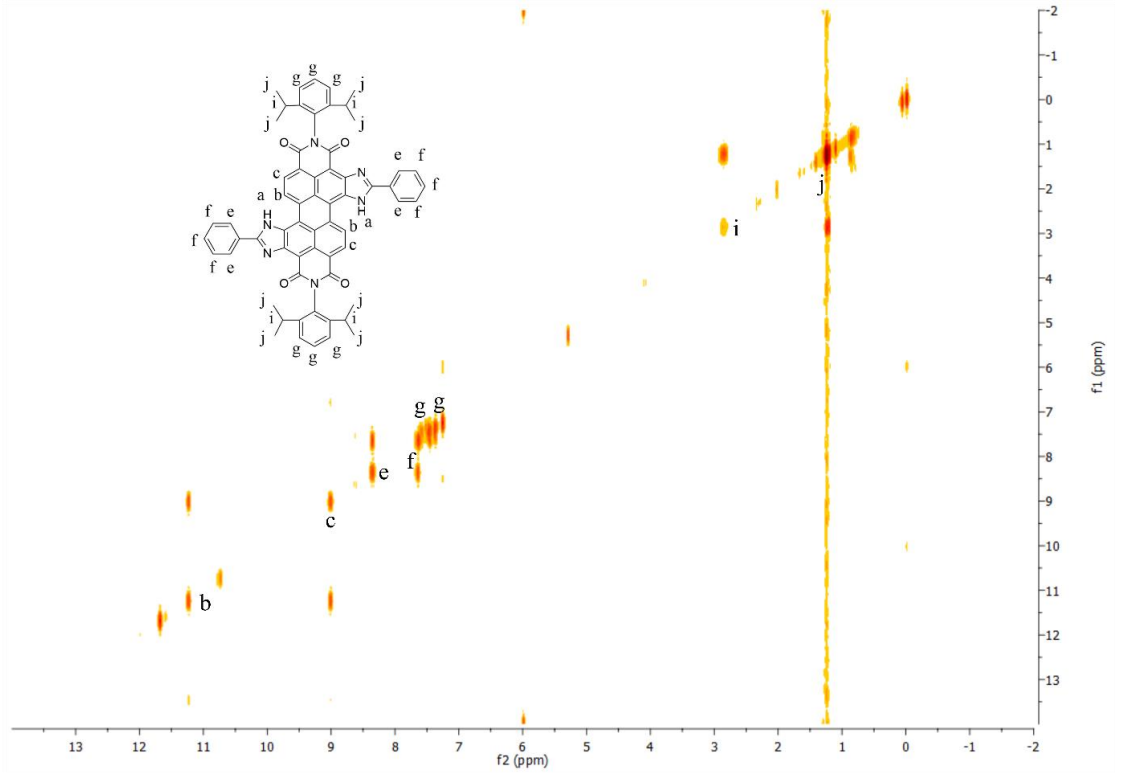

Figure S26. Cosy NMR ($CDCl_3$, 500 MHz) of **3a**.

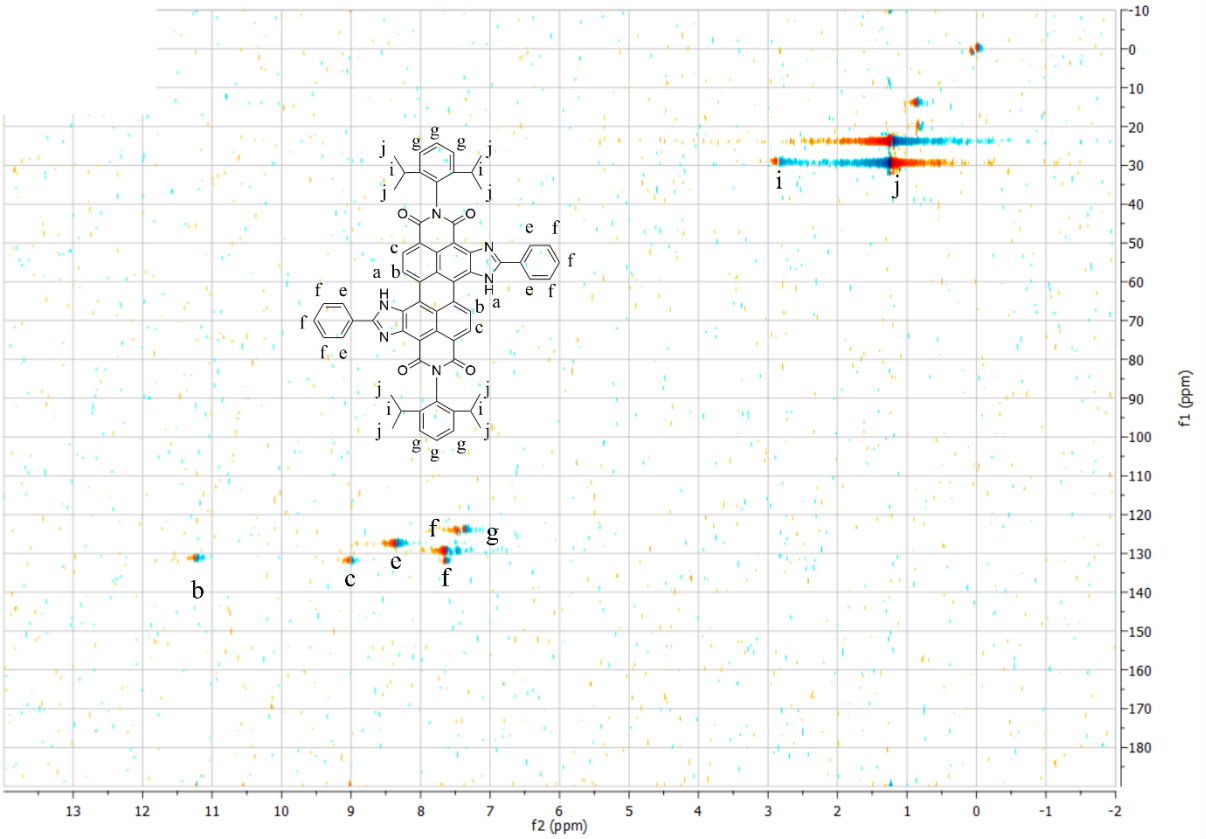

Figure S27. HSQC NMR ($CDCl_3$, 500 MHz, 126 MHz) of **3a**.

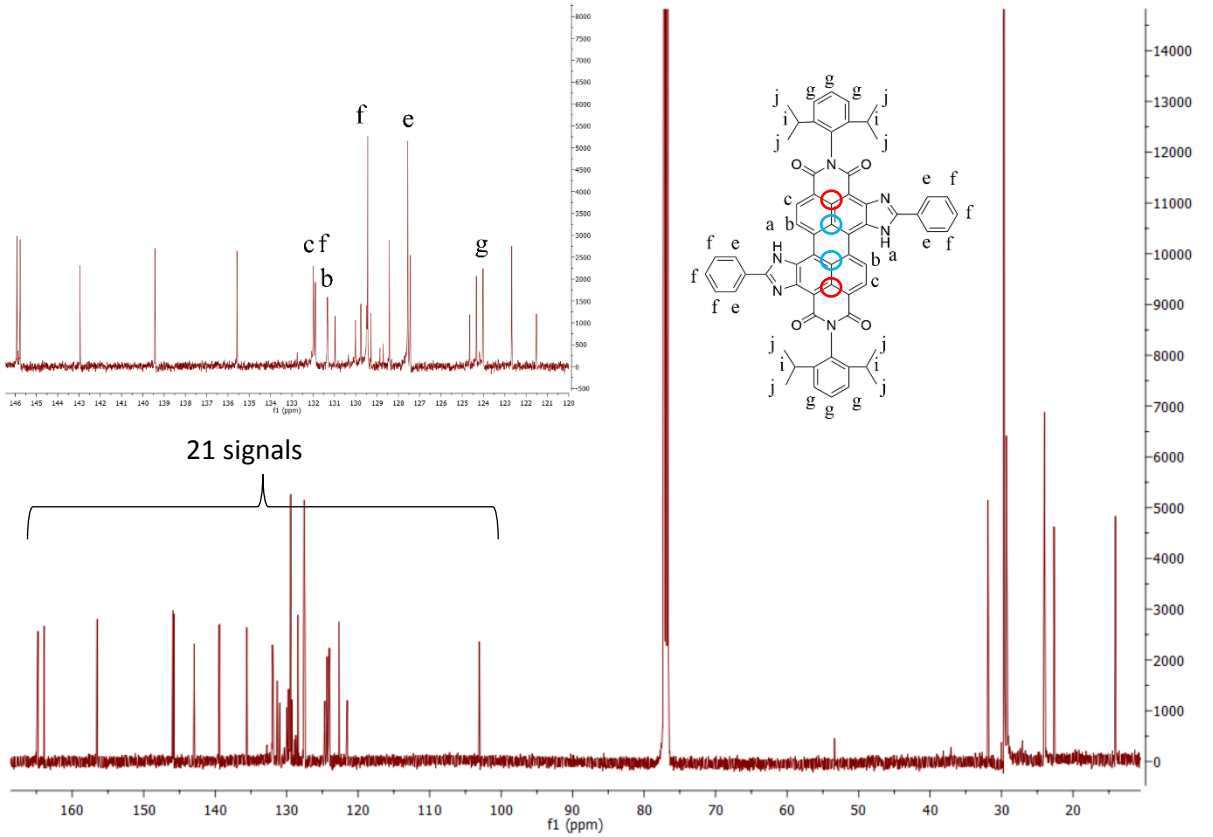

Figure S28. ^{13}C NMR ($CDCl_3$, 126 MHz) of **3a** showing overall 21 signals in the aromatic region.

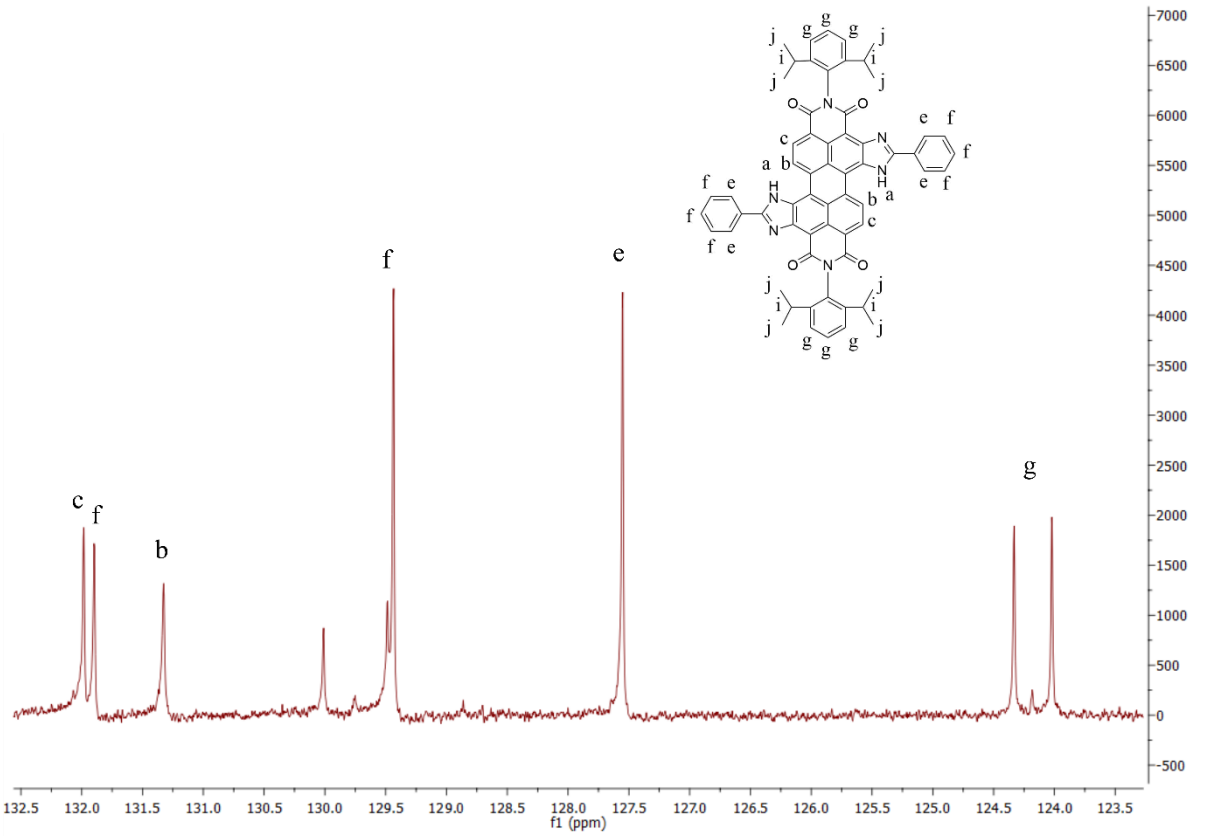

Figure S29. ^{13}C-DEPT NMR ($CDCl_3$, 126 MHz) of **3a**.

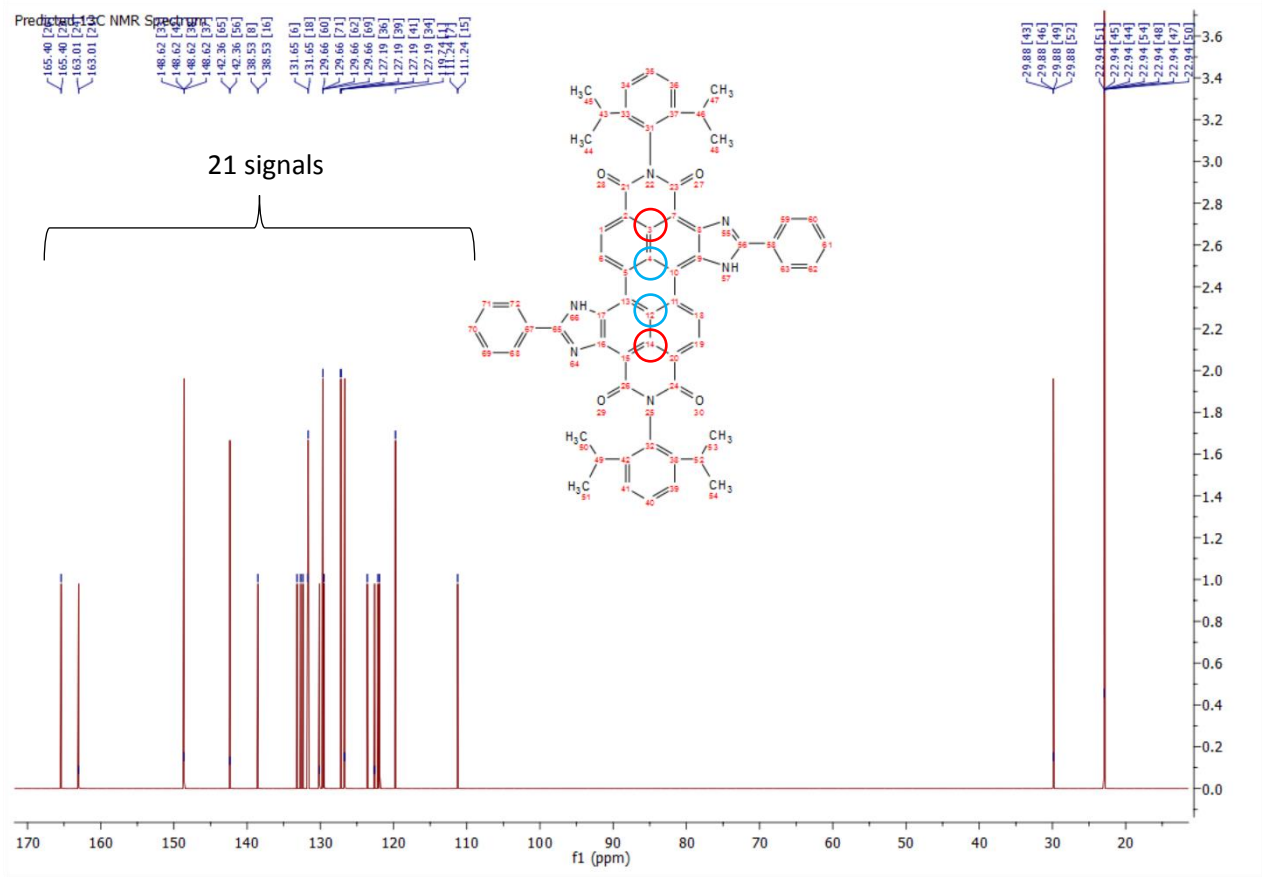

Figure S30. ^{13}C NMR simulation for symmetric **3a** with 21 signals in the aromatic region. 4 C-atoms in the centre of the perylene system (marked with red and blue circles) deliver only 2 signals due to 2 different surroundings.

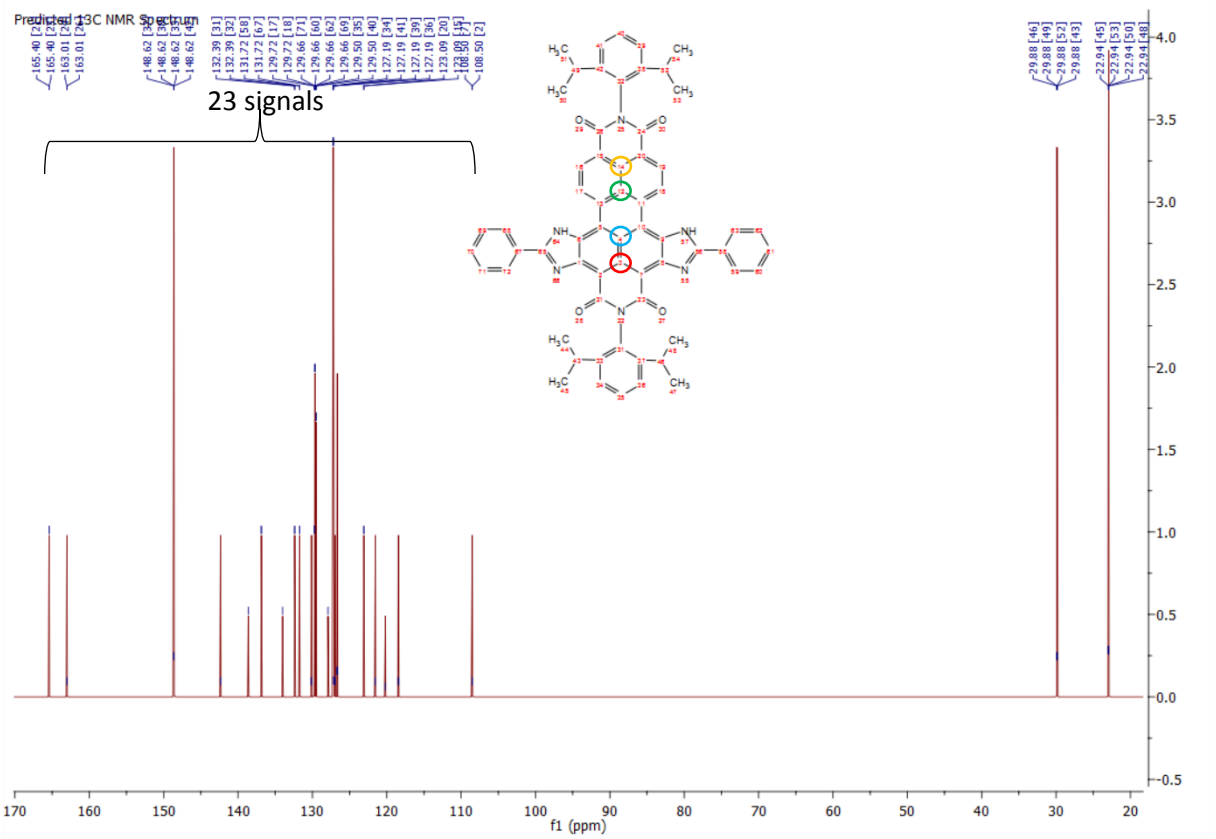

Figure S31. ^{13}C NMR simulation of **3a** regioisomer with 23 signals in the aromatic region. 4 C-atoms in the centre of the perylene system (marked with red, blue, green and yellow circles) deliver 4 signals due to 4 different surroundings.

MALDI-TOF-MS

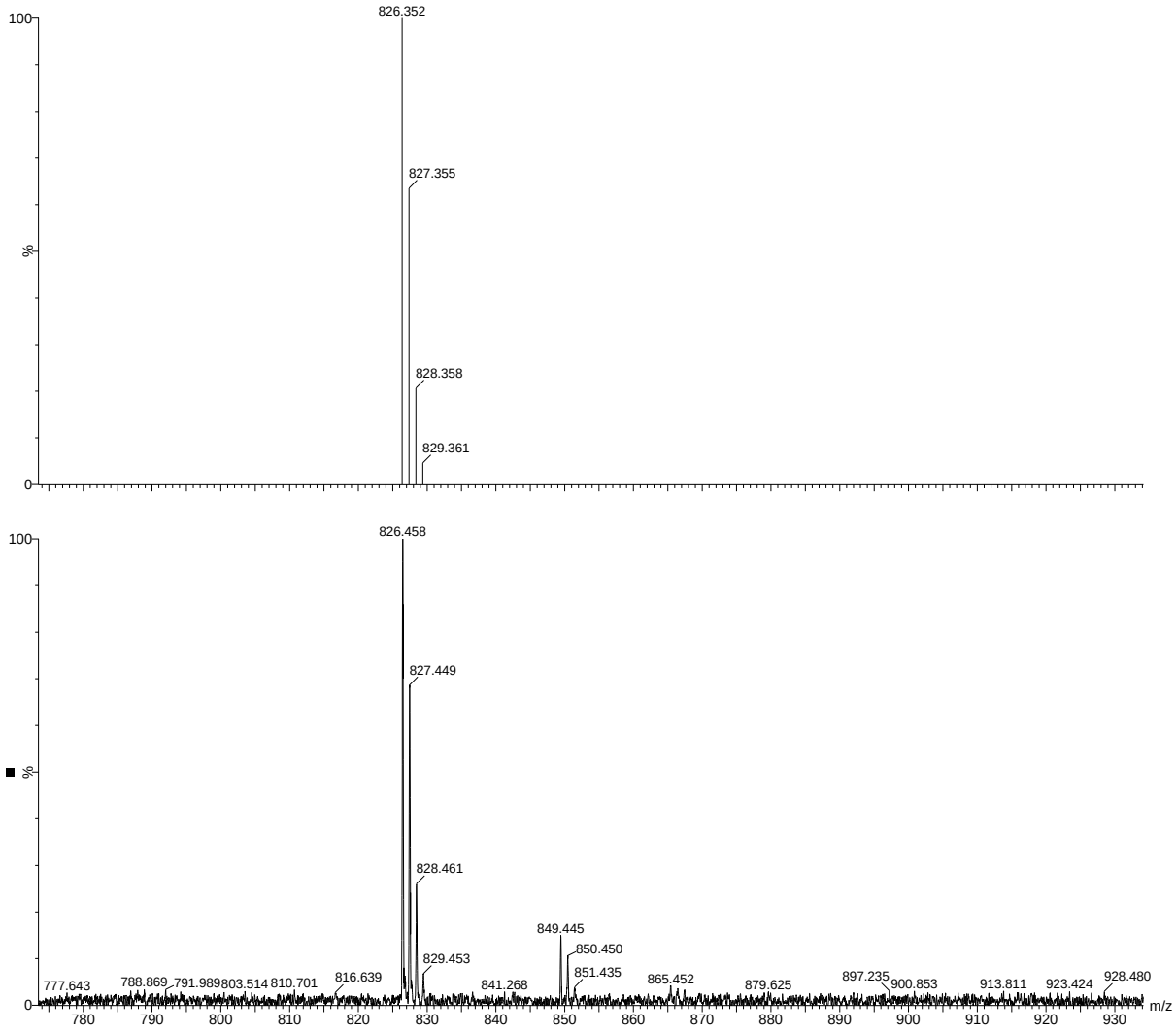

Figure S32. Theoretical isotope pattern and experimental MALDI-TOF-Mass spectrum of **2a**.

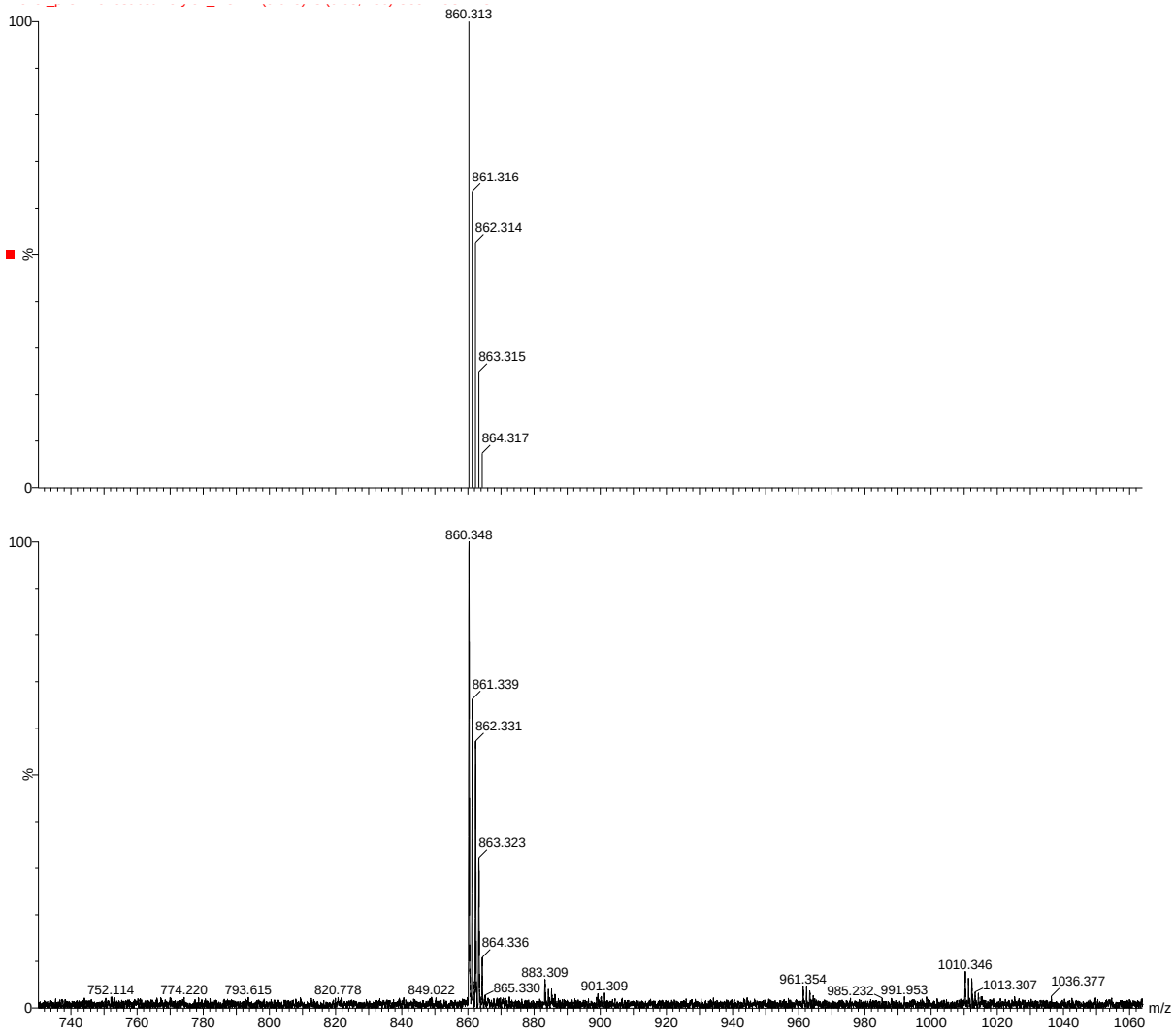

Figure S33. Theoretical isotope pattern and experimental MALDI-TOF-Mass spectrum of **2b**.

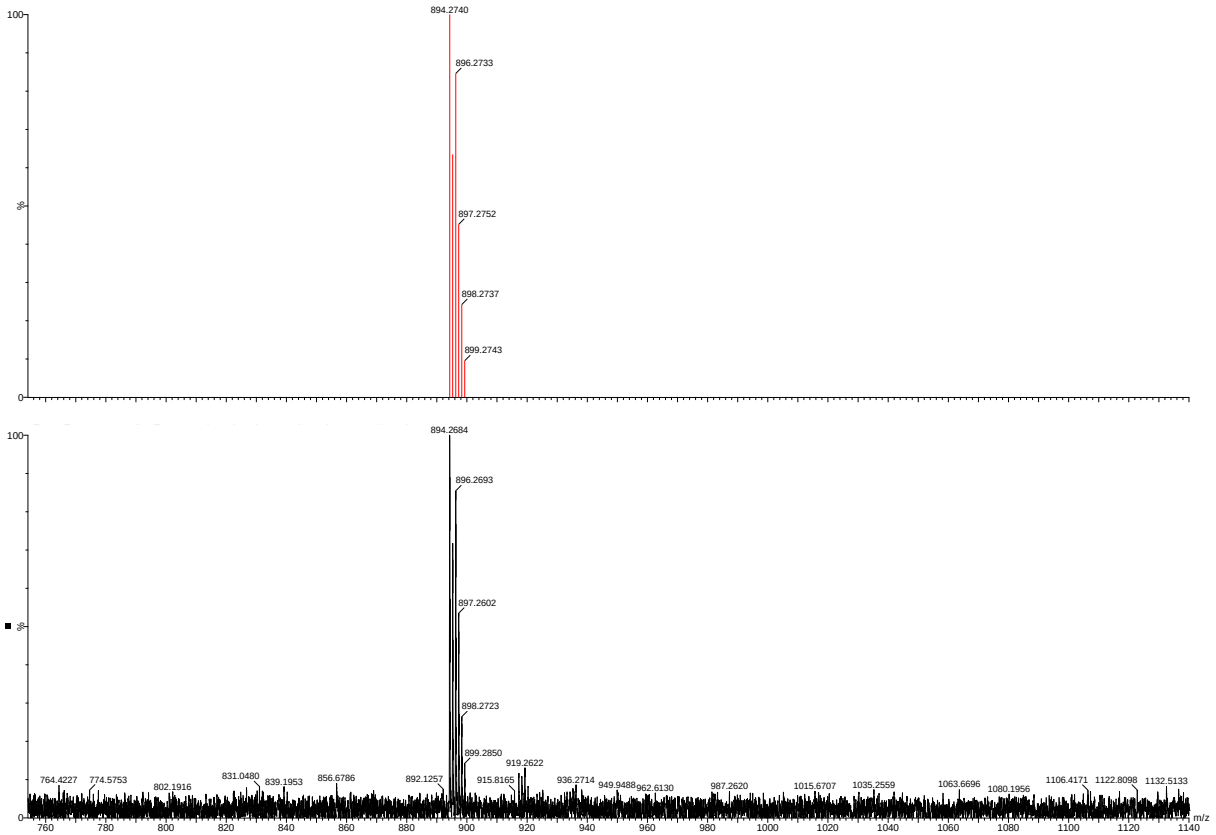

Figure S34. Theoretical isotope pattern and experimental MALDI-TOF-Mass spectrum of **2c**.

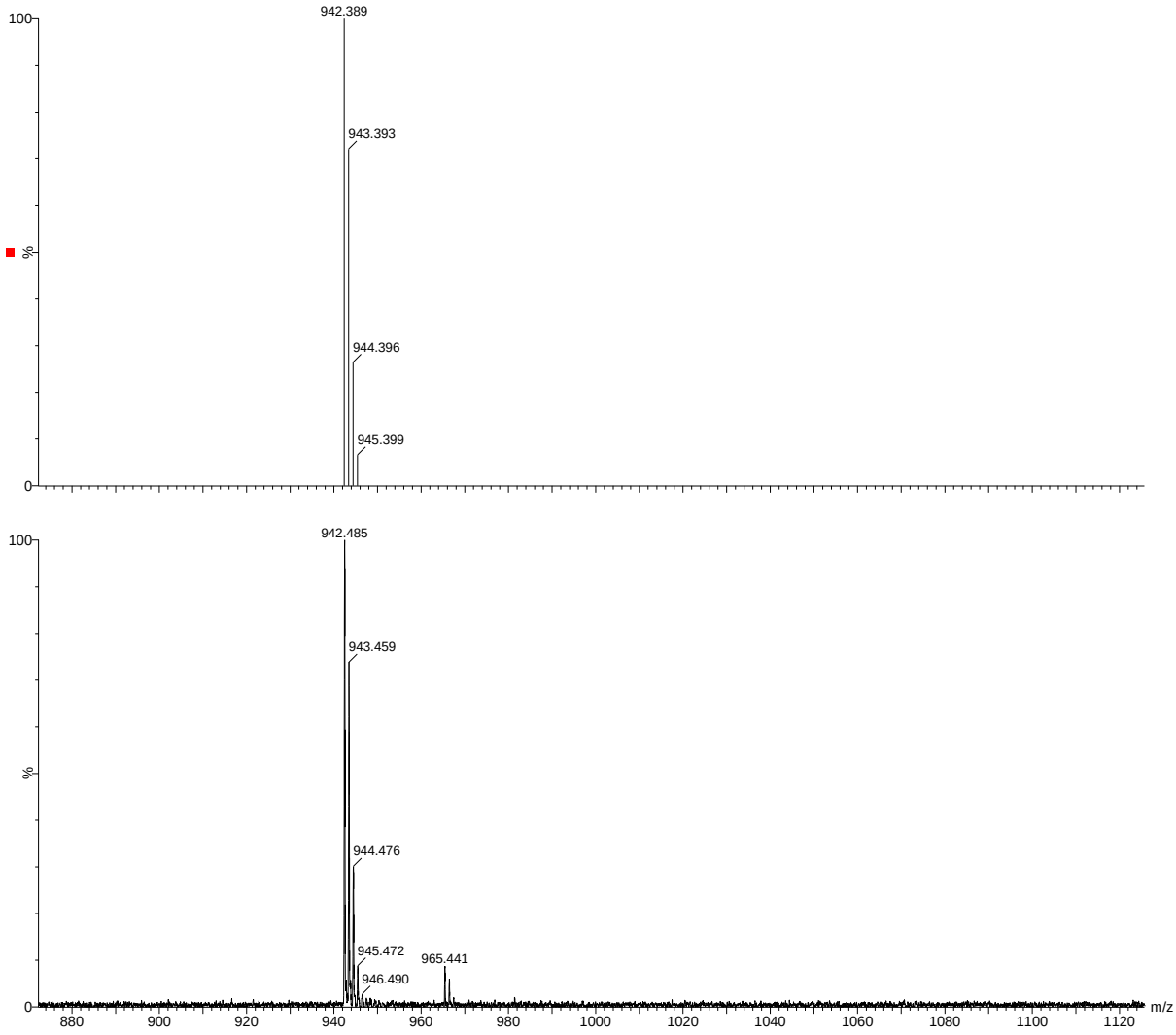

Figure S35. Theoretical isotope pattern and experimental MALDI-TOF-Mass spectrum of **3a**.