# Room temperature phosphorescence and static excimer excitation of pyrene-modified (*NCN*) pincer bismuth complexes

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## Supporting Information

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# General

All syntheses were performed under a nitrogen inert gas atmosphere and protection from light, using standard Schlenk techniques. No uncommon hazards are involved, apart from those concomitant with work under cryogenic conditions (-70 °C, cooling baths with *iso*-propanol and dry ice; appropriate protective gloves should be worn) and the use of *t*-BuLi (appropriate protective clothing should be worn; handling and storage should be carried out exclusively under inert gas condition; protection from water and moisture should be guaranteed at all times; suitable fire extinguishing agents should be held available when handling this highly flammable chemical). 1,3-Dibromo-7-(*tert*-butyl)-pyrene[1] and **(*NCN*)BiCl$_2$**[2] were prepared according to literature-known procedures.

**NMR Spectroscopy:** $^1$H-NMR (400 MHz) and $^{13}$C{$^1$H}-NMR (101 MHz) spectra were recorded in $CDCl_3$ or $CD_2Cl_2$ at 300 K using a Bruker Avance III 400 spectrometer. NMR spectra were referenced to residual protonated solvent signals ($^1$H) or to the solvent signal itself ($^{13}$C). The assignment of signals is based on 2D NMR spectra. **Mass Spectrometry:** Mass spectra were recorded in the positive ion mode on an ESI-calibrated LTQ Orbitrap Velos Spectrometer with the direct injection of acetonitrile solutions.

**X-Ray Crystallography:** A STOE IPDS-II image plate diffractometer equipped with a Mo-Kα or Cu-Kα radiation source was used. Data acquisition was conducted at 100 K. The program package X-Area was used for data processing. Either semiempirical or spherical absorption corrections were performed. The structures were solved and refined with SHELXT[3, 4] and OLEX2.[5] All non-hydrogen atoms were refined anisotropically. Crystallographic data for the structures **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 2377089 and 2377088.

**DFT and TD-DFT calculations:** The ground state electronic structures of the full models of complexes **1** and **2** were calculated by density functional theory (DFT) methods using the Gaussian 16 program packages.[6] Geometry optimization followed by vibrational analysis was performed in solvent media. Solvent effects were described by the SMD variation of IEFPCM implemented in the Gaussian program package with standard parameters for dichloromethane.[7] The fully relativistic small-core multiconfiguration Dirac Hartree-Fock-adjusted pseudopotentials and the corresponding optimized set of basis functions for Bi (ECP60MDF)[8] and 6-31G(d) polarized double-ζ basis sets[9] for the remaining atoms were employed together with the Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0).[10, 11] The GaussSum program package was used to analyze the results,[12] while the visualization of the results was performed with the Avogadro program package.[13] Graphical representations of molecular orbitals were generated with the help of GNU Parallel[14] and plotted using the vmd program package[15] in combination with POV-Ray.[16]

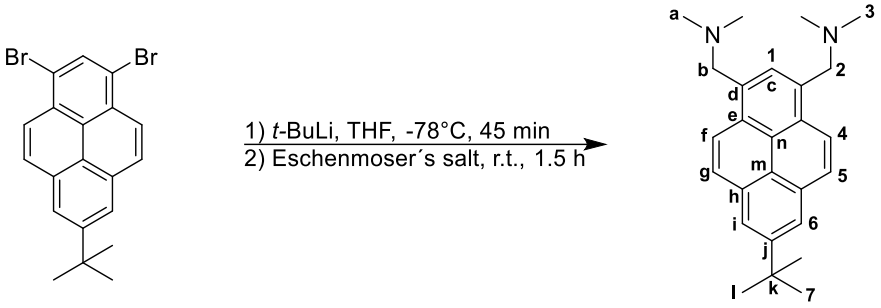
**UV/Vis Spectroscopy:** UV/Vis/NIR spectra of $CH_2Cl_2$ and MeTHF solutions of ligand ***NCHN*$_{pyr}$**, as well as complexes **1** and **2** were recorded on a TIDAS fiber optic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from J&M in HELLMA quartz cuvettes with 1.0 cm optical path lengths.

**Photoluminescence:** Luminescence spectra and lifetimes of MeTHF and $CH_2Cl_2$ solutions of the respective compound were measured on a PicoQuant FluoTime 300 spectrometer. Absolute

quantum yields were determined with an integrating sphere within the FluoTime 300 spectrometer. Solutions were deaerated through three cycles of freeze-pump-thaw.

# Synthesis

### Ligand *NCHN*$_{pyr}$

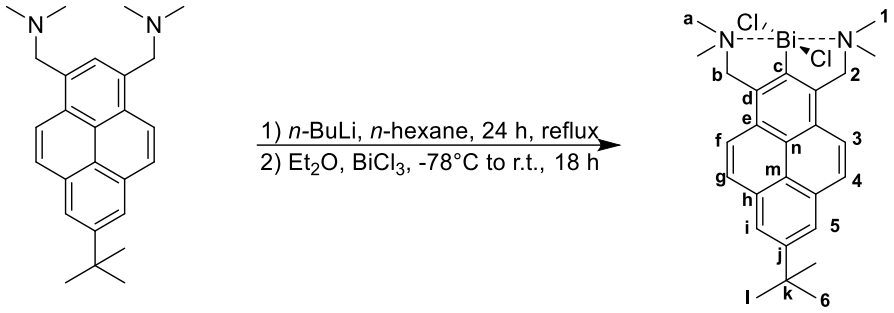



A solution of 1,3-dibromo-7-(*tert*-butyl)-pyrene[1] (2.00 g, 4.81 mmol, 1.00 eq) in 70 mL of THF was cooled to -78 °C. 10.1 mL of a 1.9 M *n*-pentane solution of *t*-BuLi (19.2 mmol, 4.00 eq) was slowly added and the mixture was stirred for 45 min at -78 °C. Then, Eschenmoser's salt (4.07 g, 22.00 mmol, 4.60 eq) was added and the reaction mixture was allowed to warm to r.t. and stirred for 90 min. THF was removed *in vacuo* and the reaction was quenched with water (50 mL). 50 mL of EtOAc were added and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 25 mL), the organic phases were combined, dried over $MgSO_4$, and the solvent was removed *in vacuo*. Impurities could be removed by column chromatography with $CH_2Cl_2$ as the eluent. The product remained on the top of the column and could be extracted from the silica gel with a $CH_2Cl_2$/$NEt_3$ solution (1:1). ***NCHN*$_{pyr}$** was obtained as an orange solid (1.59 g, 4.27 mmol, 89% yield).

**$^1$H-NMR** ($CDCl_3$, 400 MHz) δ [ppm]: 8.49 (d, $^3J_{HH}$ = 9.1 Hz, 2H, $H^5$), 8.26 (s, 2H, $H^6$), 8.11 (d, $^3J_{HH}$ = 9.4 Hz, 2H, $H^4$), 7.91 (s, 1H, $H^1$), 4.10 (s, 4H, $H^2$), 2.38 (s, 12H, $H^3$), 1.63 (s, 9H, $H^7$).

**$^{13}$C-NMR** ($CDCl_3$, 101 MHz) δ [ppm]: 148.9 ($C^j$), 131.7 ($C^h$), 131.0 ($C^d$), 130.3 ($C^c$), 129.4 ($C^e$), 127.4 ($C^f$), 125.5 ($C^n$), 123.8 ($C^g$), 123.3 ($C^m$), 122.4 ($C^i$), 62.5 ($C^b$), 45.7 ($C^a$), 35.2 ($C^k$), 32.0 ($C^l$).

**ESI-MS** $C_{26}H_{32}N_2^+$, Calc. 372.2565, Found 372.2687, $C_{22}H_{24}N_2^+$, Calc. 316.1939, Found 316.2048, $C_{21}H_{19}^+$, Calc. 271.1481, Found 271.1484.




Synthesis and the purification were carried out under inert gas conditions. ***NCHN*$_{\mathbf{pyr}}$** (0.76 g, 1.54 mmol, 1.00 eq) was dissolved in 5 mL of *n*-hexane and *n*-BuLi (0.94 mL of a 1.6 M solution in *n*-hexane, 1.50 mmol, 1.00 eq) was added. The reaction mixture was heated to reflux for 24 h. Then, the solvent was removed *in vacuo*. The remaining solid was dissolved with 15 mL $Et_2O$ and the resulting solution was slowly transferred by a cannula into a solution of $BiCl_3$ (0.48 g, 1.53 mmol, 1.00 eq) in 10 mL of $Et_2O$, which was precooled to -78 °C. After stirring for 1 h the reaction mixture was warmed to room temperature and stirred for 18 h. The solvent was removed *in vacuo*. The remaining solid was extracted with $CH_2Cl_2$. The insoluble solid was filtered off. Afterwards, the solution was stripped of the solvent *in vacuo*. The remaining solid was washed with *n*-hexane and then dried *in vacuo*. Complex **1** was was obtained as a yellow-beige solid (244 mg, 0.38 mmol, 25%).

**$^1$H-NMR** ($CD_2Cl_2$, 400 MHz) δ [ppm]: 8.30 (s, 2H, $H^5$), 8.22 (d, $^3J_{HH}$ = 9.2 Hz, 2H, $H^3$), 8.19 (d, $^3J_{HH}$ = 9.2 Hz, 2H, $H^4$), 5.32 (s, 4H, $H^2$), 3.07 (s, 12H, $H^1$), 1.60 (s, 9H, $H^6$).

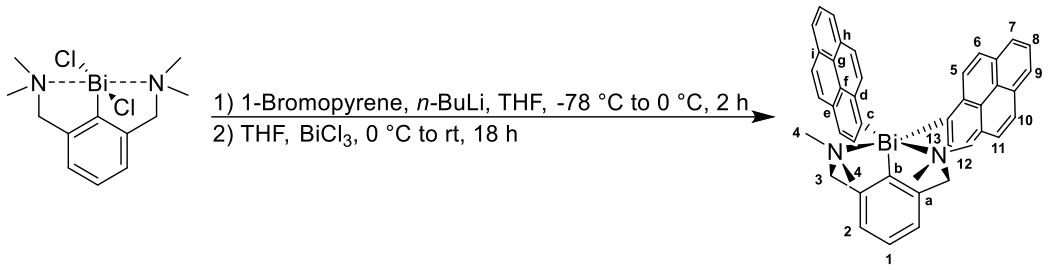
**$^1$H-NMR** ($CDCl_3$, 400 MHz) δ [ppm]: 8.25 (s, 2H, $H^5$), 8.16 (m, 4H, $H^{3,4}$), 5.34 (s, 4H, $H^2$), 3.10 (s, 12H, $H^1$), 1.59 (s, 9H, $H^6$).

**$^{13}$C-NMR** ($CD_2Cl_2$, 101 MHz) δ [ppm]: 207.3 ($C^c$), 150.3 ($C^j$), 144.0 ($C^e$), 132.2 ($C^d$), 131.1 ($C^h$), 129.6 ($C^g$), 125.6 ($C^n$), 124.4 ($C^f$), 123.7 ($C^i$), 123.6 ($C^m$), 66.1 ($C^b$), 48.2 ($C^a$), 35.6 ($C^k$), 32.0 ($C^l$).

**$^{13}$C-NMR** ($CDCl_3$, 101 MHz) δ [ppm]: 207.1 ($C^c$), 149.9 ($C^j$), 143.5 ($C^e$), 132.1 ($C^d$), 131.0 ($C^h$), 129.6 ($C^g$), 125.6 ($C^n$), 124.0 ($C^f$), 123.5 ($C^{i,m}$), 66.0 ($C^b$), 48.1 ($C^a$), 35.4 ($C^k$), 32.0 ($C^l$).

**ESI-MS** $BiC_{26}H_{31}N_2Cl^+$, Calc. 615.1974, Found 615.2006, $Bi_2C_{52}H_{62}N_4Cl_3^+$, Calc. 1265.3642, Found 1265.3714.

The sample for combustion analysis was obtained by extracting the solid into 25 mL of benzene, filtering, and drying in vacuo to yield the compound as benzene monosolvate. **Elemental analysis** Calc. for $C_{26}H_{31}BiCl_2N_2 \times C_6H_6$: C, 52.68; H, 5.11; N, 3.84. Found: C, 52.60; H, 5.47; N, 3.64.




Synthesis and the purification were carried out under inert gas conditions. 1-Bromopyrene (280 mg, 1.00 mmol, 2.00 eq) was dissolved in 5 mL of dry THF and the solution was cooled to -78 °C. A 2.5 M solution of *n*-BuLi (0.499 mL, 1.25 mmol, 2.50 eq) in hexane was added dropwisely. The orange reaction mixture was stirred for 2 h and warmed to 0 °C. **(*NCN*)BiCl$_2$** (235 mg, 0.500 mmol, 1.00 eq) was suspended in 20 mL of dry THF and the suspension was cooled to 0 °C. The lithiated species was added dropwisely to the suspension. The yellow reaction mixture was stirred for 1 h at 0 °C and for 18 h at room temperature. The solvent was removed *in vacuo*. The solid was washed with 20 mL of *n*-hexane and 90 mL of acetonitrile and then dried *in vacuo*. The remaining solid was extracted with benzene. The solution was filtered and the solvent was evaporated to yield **2** as a beige solid (208 mg, 0.26 mmol, 52%).

**$^1$H-NMR** ($CD_2Cl_2$, 400 MHz) δ [ppm] = 8.99 (d, 2H, $H^{10}$, $^3J_{HH}$ = 7.6 Hz), 8.82 (d, 2H, $H^9$, $^3J_{HH}$ = 9.2 Hz), 8.10-8.03 (m, 6H, $H^{7\text{-}8,10\text{-}13}$), 7.96 (d, 2H, $H^{11}$, $^3J_{HH}$ = 7.6 Hz), 7.90-7.85 (m, 6H, $H^{7\text{-}8,10\text{-}13}$), 7.40 (t, 1H, $H^1$, $^3J_{HH}$ = 6.6 Hz), 7.32 (d, 2H, $H^2$, $^3J_{HH}$ = 7.3 Hz), 3.32 (s, 4H, $H^3$), 1.73 (s, 12H, $H^4$).

**$^{13}$C-NMR** ($CD_2Cl_2$, 101 MHz) δ [ppm]: 166.2, 149.8, 137.5, 136.6, 132.2, 131.8, 131.5, 130.2, 129.9, 128.7, 128.2, 128.1, 126.9, 126.8, 126.7, 125.9, 125.7, 125.6, 124.7, 124.6, 67.5, 44.8.

**ESI-MS** $BiC_{28}H_{28}N_2^+$, Calc. 601.2051, Found 601.2030.

**Elemental analysis** Calc. for $C_{44}H_{37}BiN_2$: C, 64.83; H, 4.65; N, 3.49. Found: C, 64.89; H, 4.86; N, 3.36.

# NMR Data

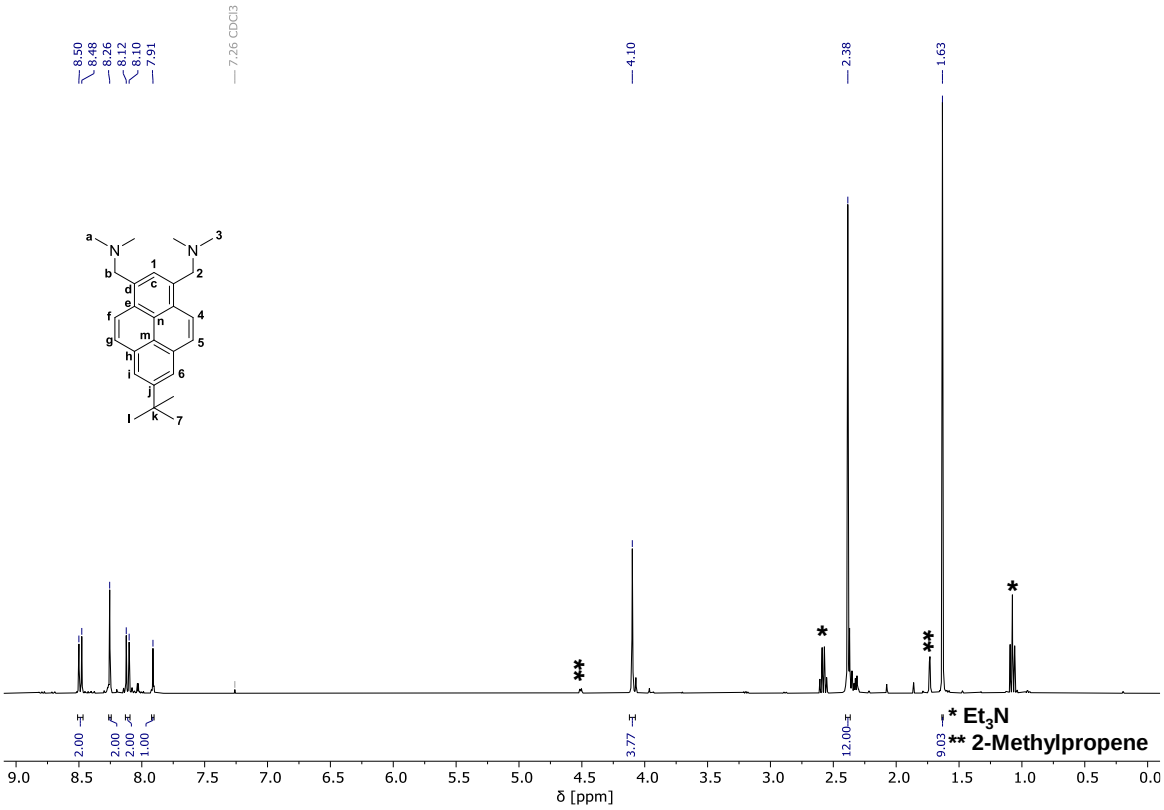



**Figure S1.** $^{1}$H-NMR spectrum of ***NCHN*$_{pyr}$**.

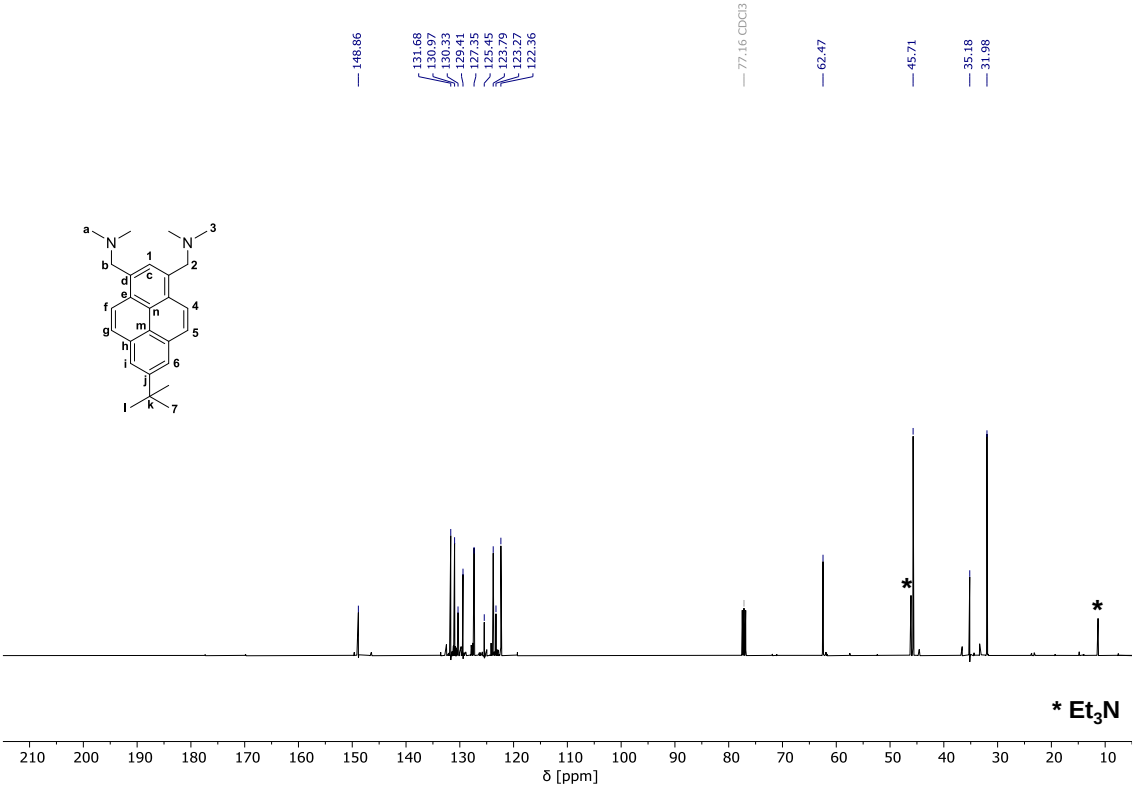



**Figure S2.** $^{13}$C-NMR spectrum of ***NCHN*$_{pyr}$**.

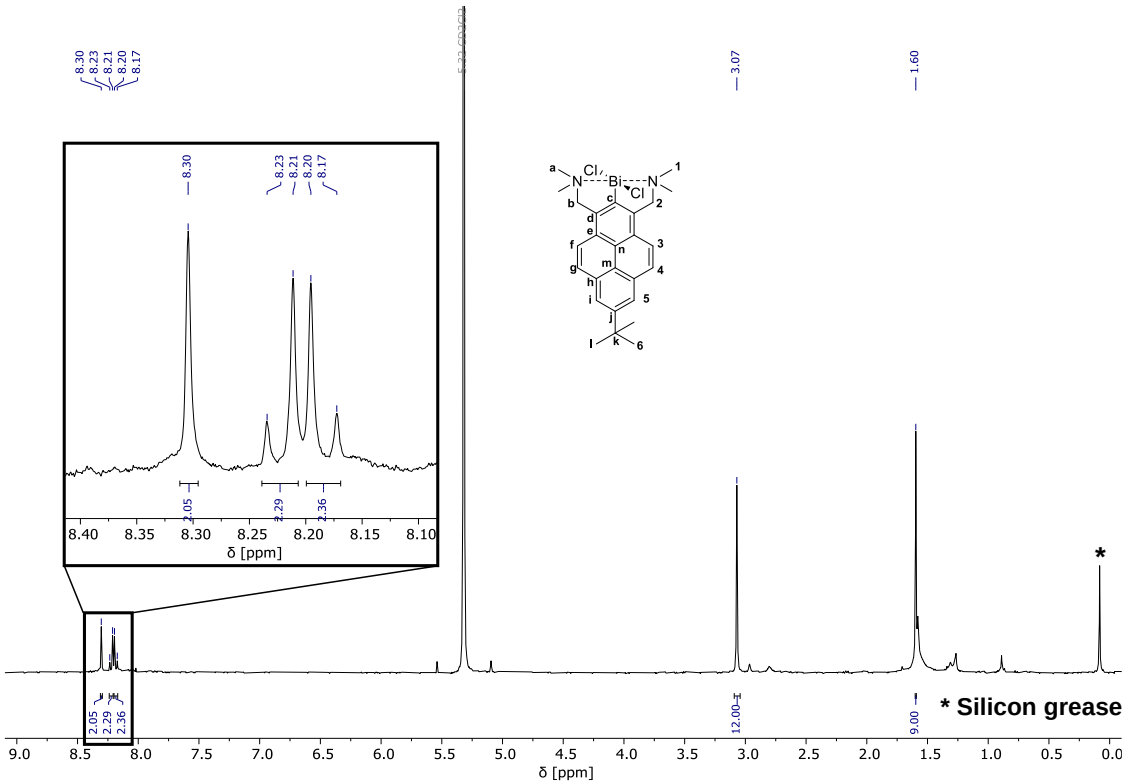



**Figure S3.** $^{1}$H-NMR spectrum of **1**.

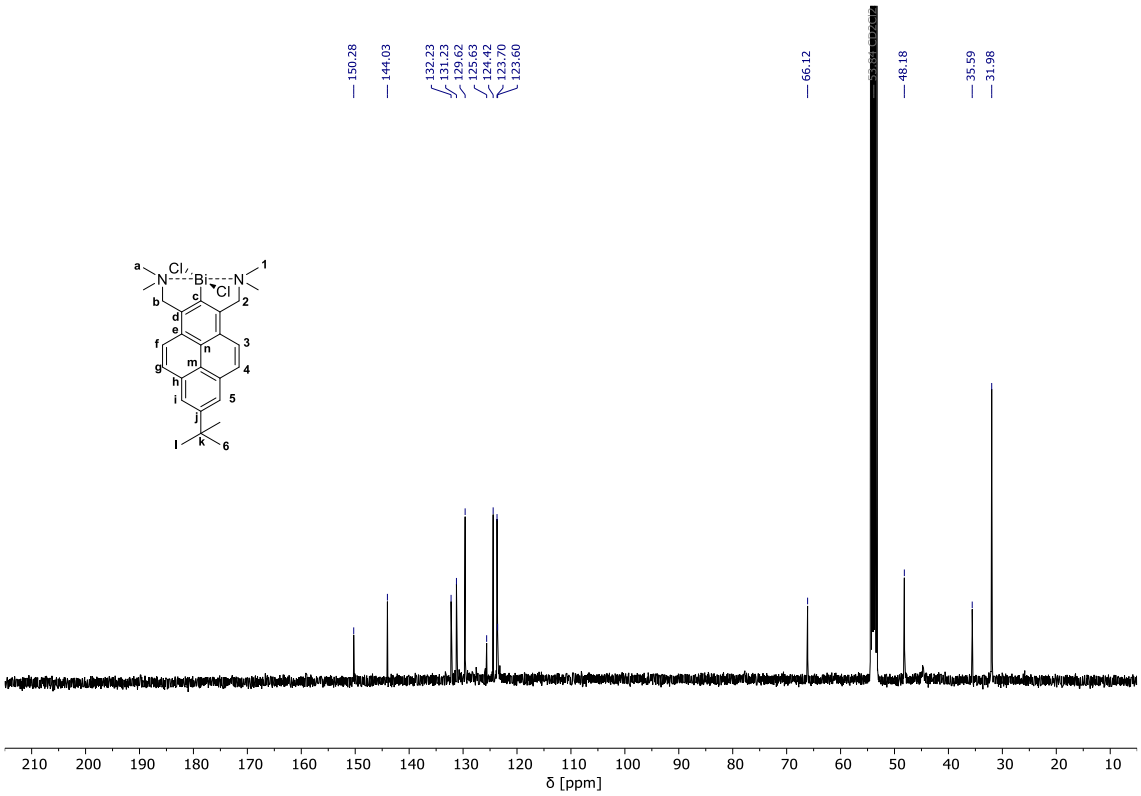



**Figure S4.** $^{13}$C-NMR spectrum of **1**.

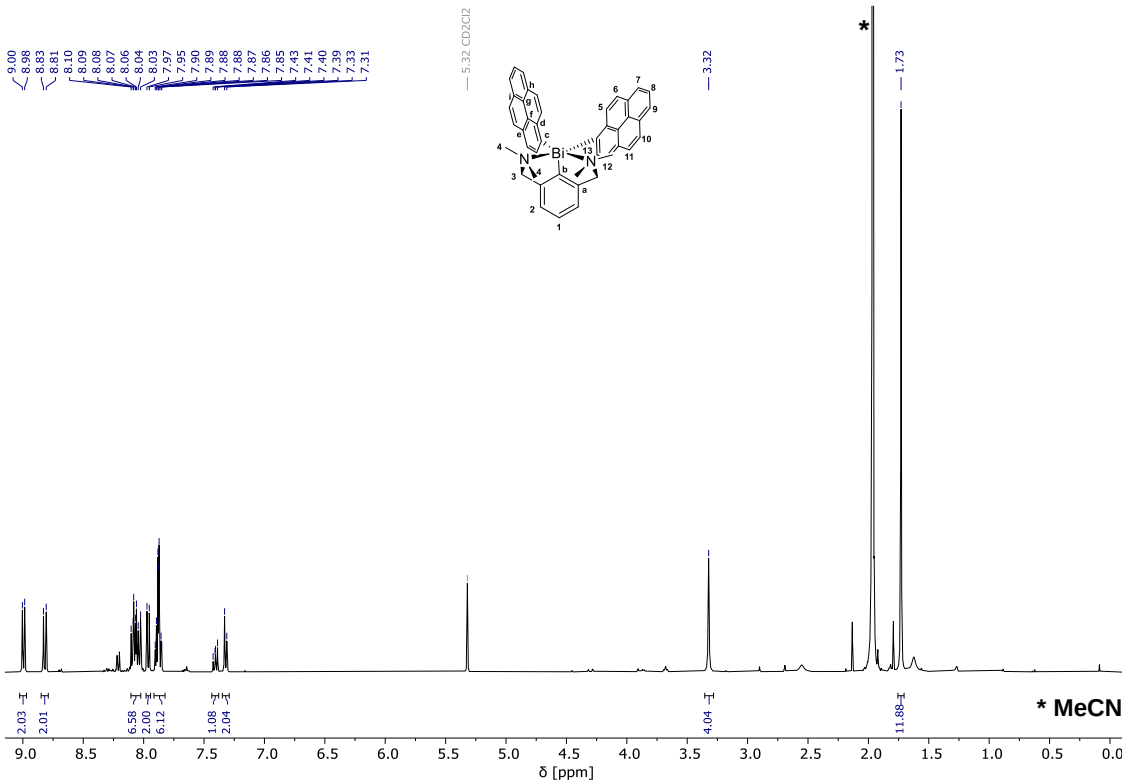



**Figure S5.** $^{1}$H-NMR spectrum of **2**.

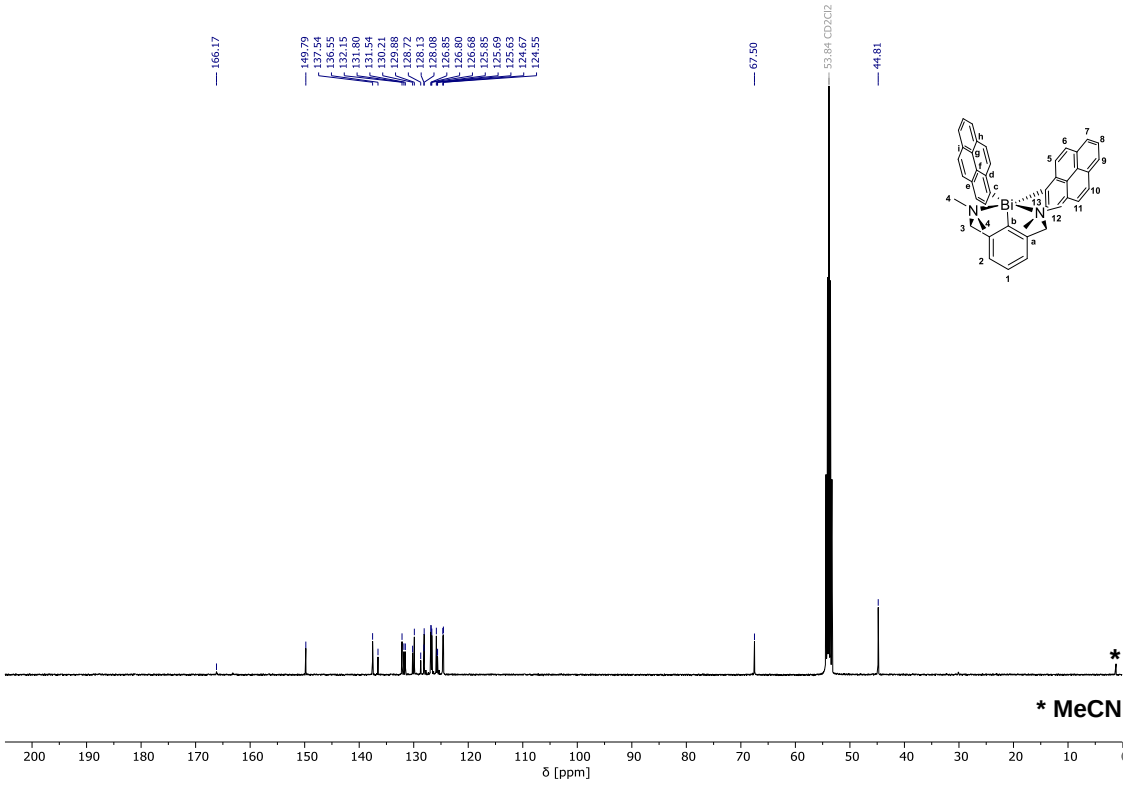



**Figure S6.** $^{13}$C-NMR spectrum of **2**.

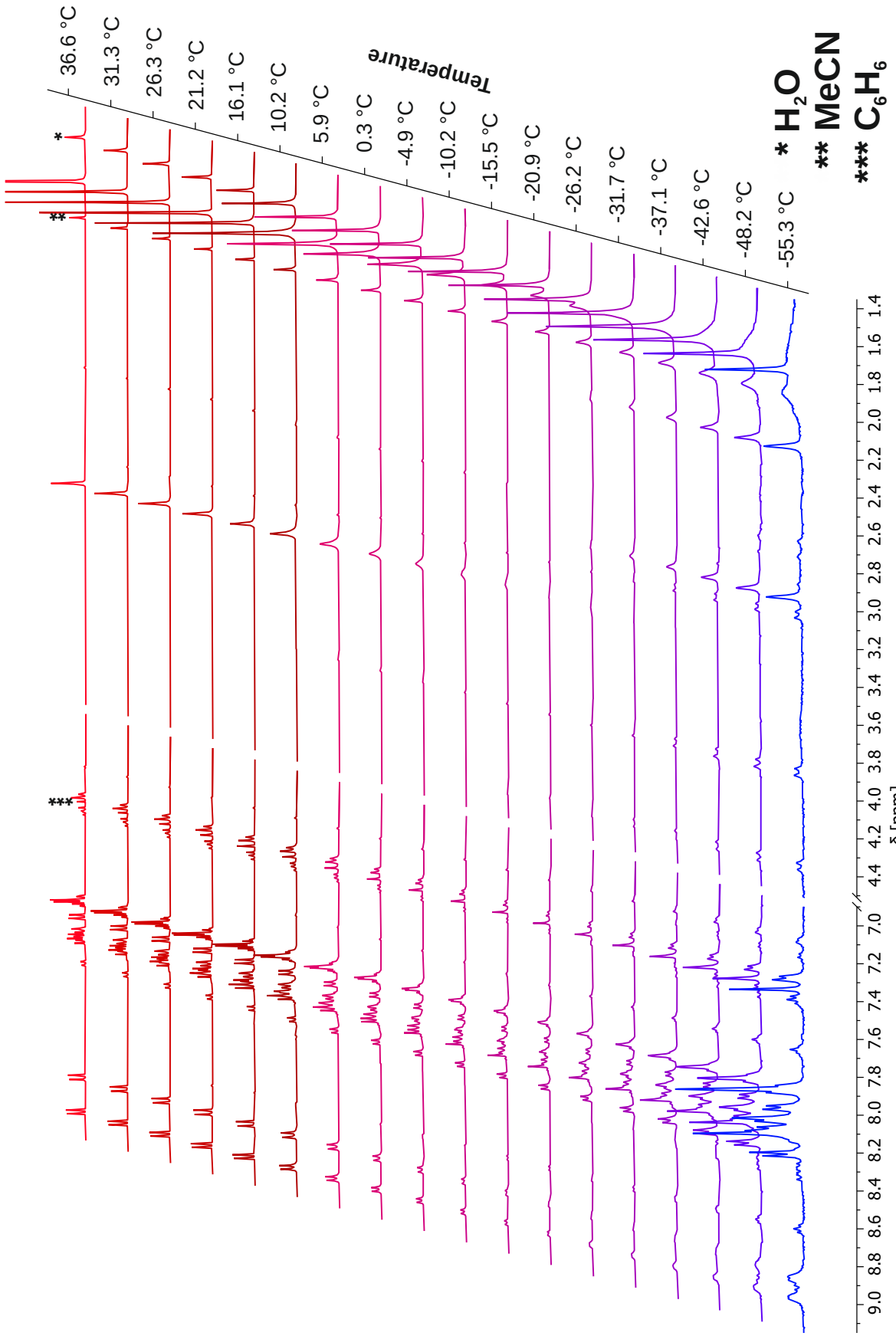



**Figure S7.** Temperature-dependent $^{1}$H-NMR spectra of **2** in $CD_2Cl_2$.

# ESI-MS Data

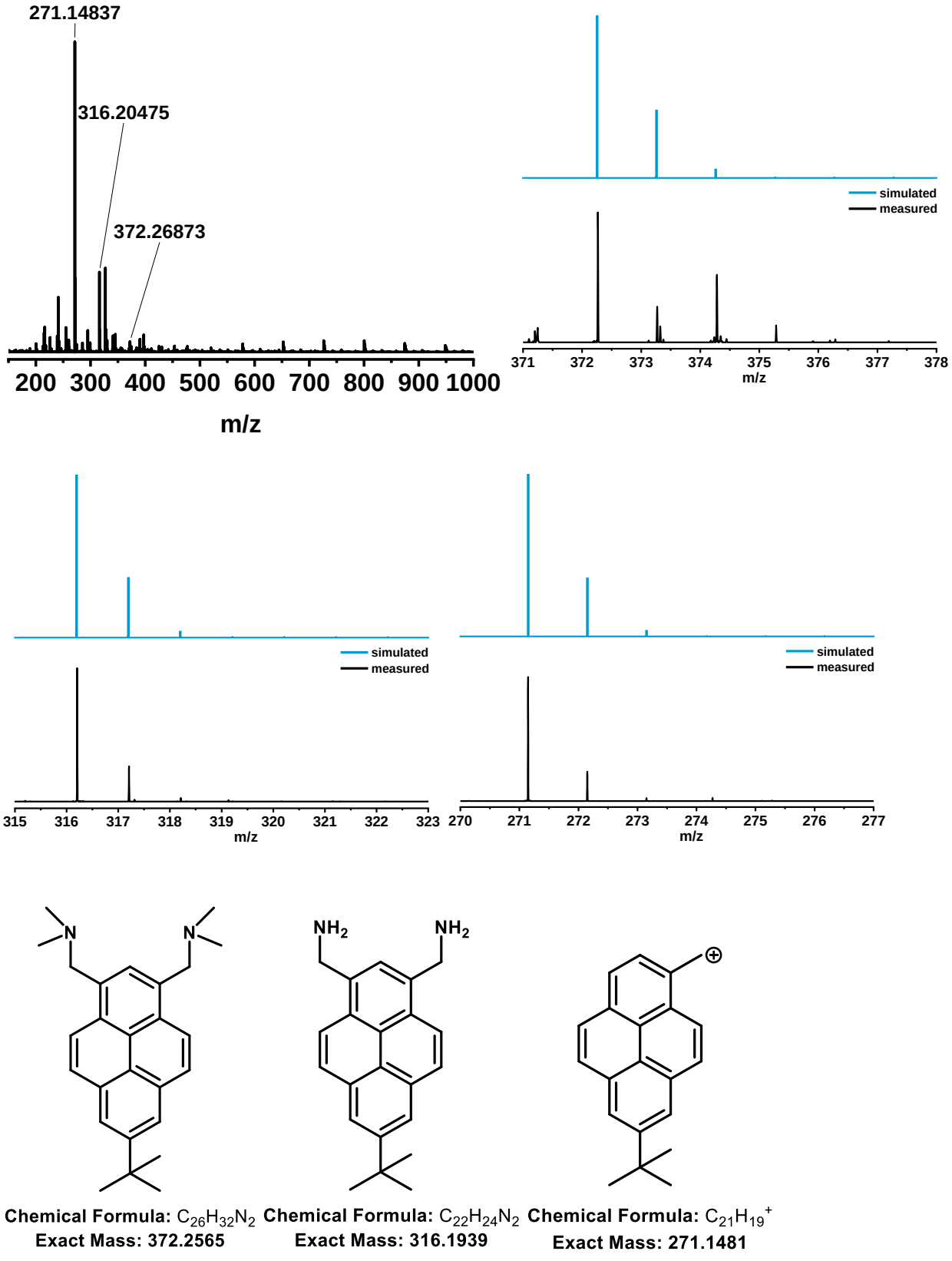
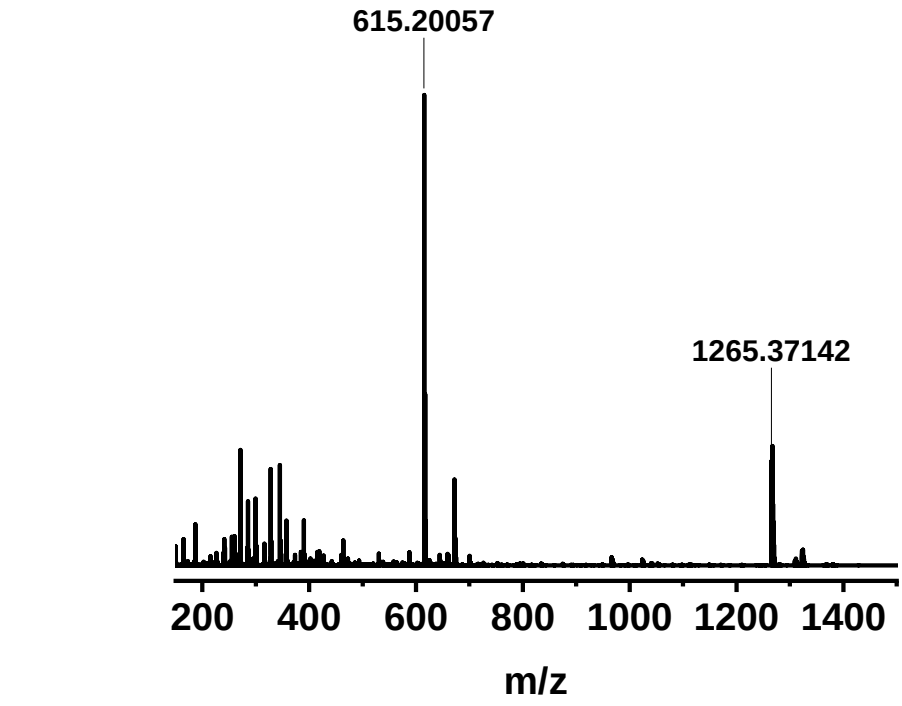
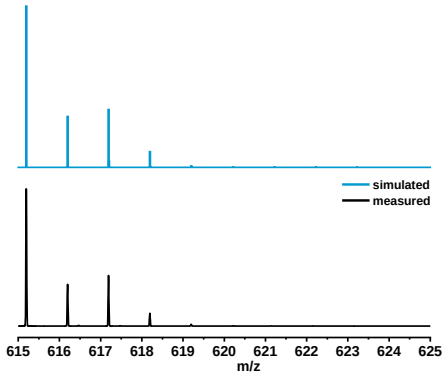
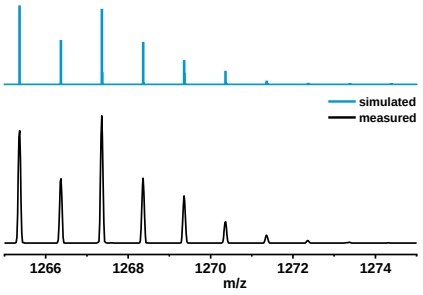
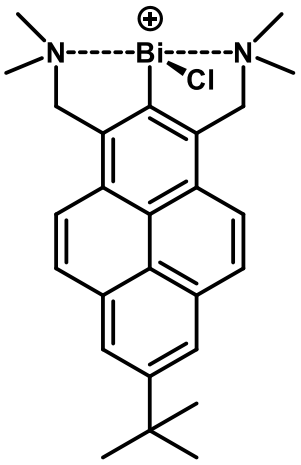



**Figure S8.** ESI-MS of ***NCHN*$_{pyr}$** (black measured, blue simulated).

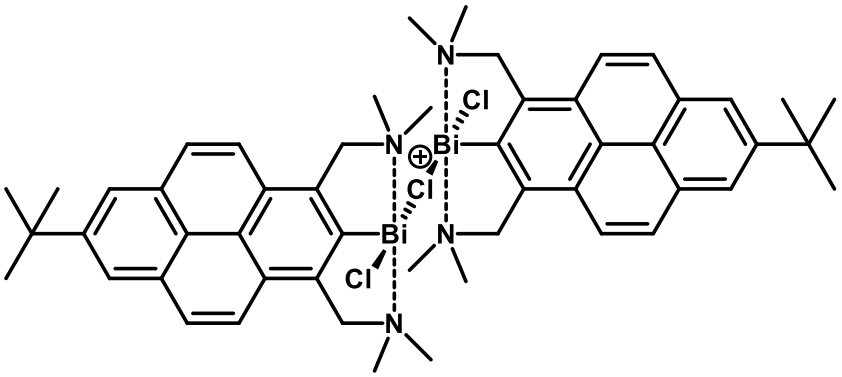



**Chemical Formula:** $C_{26}H_{31}BiClN_2^+$
**Exact Mass: 615.1974**




**Chemical Formula:** $C_{52}H_{62}Bi_2Cl_3N_4^+$
**Exact Mass: 1265.3642**

**Figure S9.** ESI-MS of complex **1** (black measured, blue simulated).

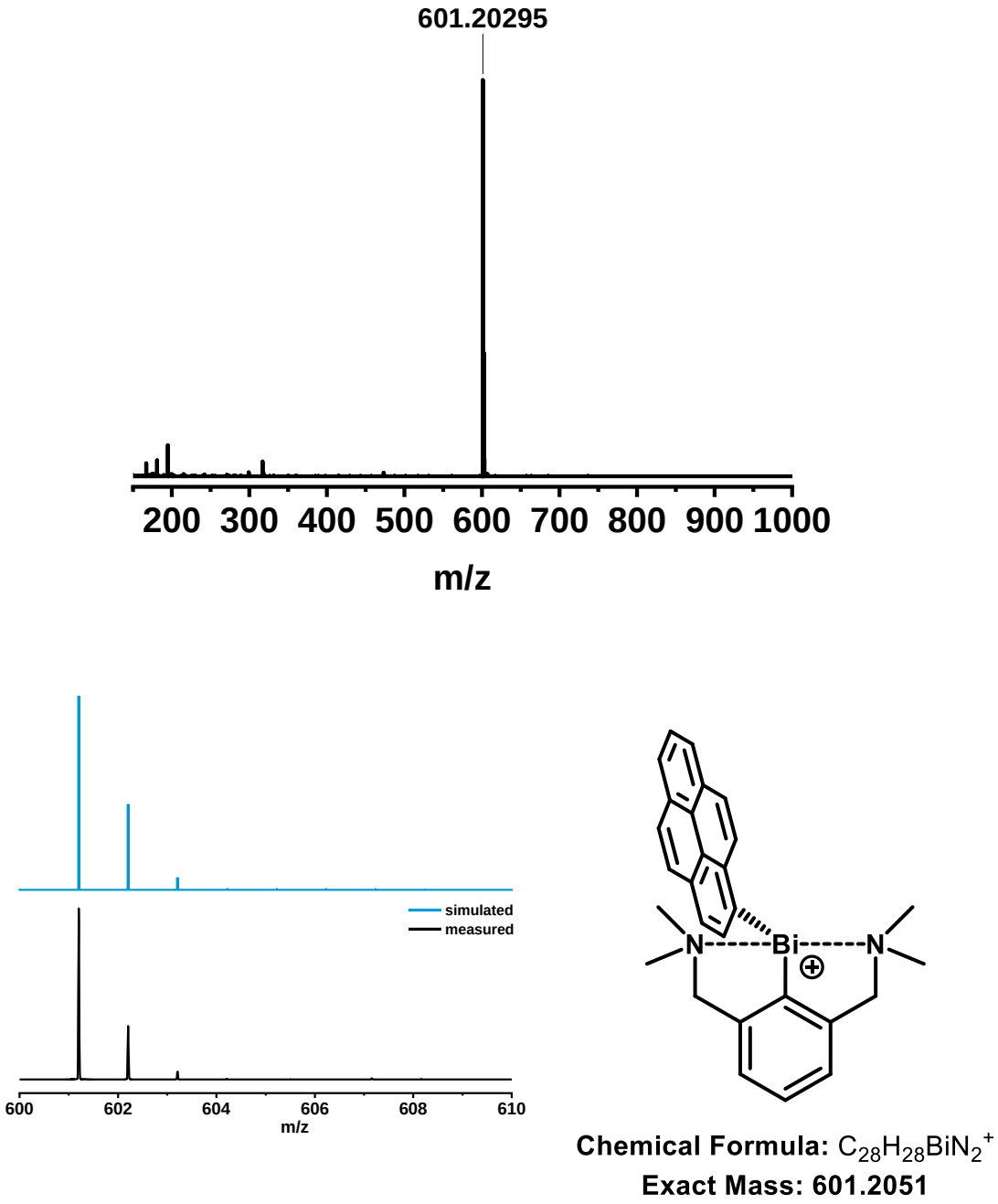



**Figure S10.** ESI-MS of complex **2** (black measured, blue simulated).

# Single Crystal X-ray Diffraction Data

**Table S1.** Crystal data and structure refinement for **1**.

| | |
|---|---|
| Identification code | **1** |
| Empirical formula | $C_{31}H_{43}BiCl_2N_2$ |
| Formula weight | 723.55 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| *a*/Å | 8.0167(3) |
| *b*/Å | 13.3464(5) |
| *c*/Å | 15.4903(6) |
| *α*/° | 113.090(3) |
| *β*/° | 92.143(3) |
| *γ*/° | 98.505(3) |
| Volume/Å$^3$ | 1499.52(10) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.602 |
| $\mu$/mm$^{-1}$ | 6.079 |
| *F*(000) | 720.0 |
| Crystal size/mm$^3$ | 0.15 × 0.1 × 0.05 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.438 to 55.104 |
| Index ranges | $-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$ |
| Reflections collected | 13209 |
| Independent reflections | 6856 [$R_{int}$ = 0.0477, $R_{sigma}$ = 0.0600] |
| Data/restraints/parameters | 6856/0/334 |
| Goodness-of-fit on $F^2$ | 1.140 |
| Final R indexes [I ≥ 2σ (I)] | $R_1$ = 0.0558, w$R_2$ = 0.1191 |
| Final R indexes [all data] | $R_1$ = 0.0827, w$R_2$ = 0.1456 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.43/-2.98 |

**Table S2.** Bond Lengths [Å] for **1**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Bi1 | Cl1 | 2.726(2) | C4 | C16 | 1.436(14) |
| Bi1 | Cl2 | 2.660(3) | C4 | C3 | 1.427(13) |
| Bi1 | N1 | 2.489(9) | C4 | C5 | 1.413(13) |
| Bi1 | N2 | 2.519(8) | C21 | C19 | 1.393(14) |
| Bi1 | C1 | 2.235(10) | C6 | C5 | 1.414(13) |
| N1 | C9 | 1.472(13) | C20 | C18 | 1.399(14) |
| N1 | C8 | 1.478(14) | C16 | C18 | 1.416(13) |
| N1 | C7 | 1.508(14) | C16 | C19 | 1.418(14) |
| N2 | C12 | 1.466(12) | C3 | C2 | 1.403(14) |
| N2 | C11 | 1.483(13) | C3 | C13 | 1.439(14) |
| N2 | C10 | 1.484(12) | C18 | C15 | 1.433(14) |
| C1 | C6 | 1.403(13) | C19 | C17 | 1.435(13) |
| C1 | C2 | 1.374(14) | C5 | C14 | 1.439(13) |
| C22 | C23 | 1.534(13) | C15 | C13 | 1.345(14) |
| C22 | C21 | 1.420(13) | C14 | C17 | 1.357(14) |
| C22 | C20 | 1.363(14) | C2 | C7 | 1.534(14) |
| C23 | C26 | 1.550(15) | C29 | C30 | 1.504(16) |
| C23 | C24 | 1.522(14) | C29 | C28 | 1.525(15) |
| C23 | C25 | 1.510(14) | C30 | C31 | 1.505(16) |

**Table S3.** Bond Angles [°] for **1**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Cl2 | Bi1 | Cl1 | 175.32(8) | C3 | C4 | C16 | 118.9(9) |
| N1 | Bi1 | Cl1 | 97.4(2) | C5 | C4 | C16 | 119.7(9) |
| N1 | Bi1 | Cl2 | 82.6(2) | C5 | C4 | C3 | 121.4(9) |
| N1 | Bi1 | N2 | 143.9(3) | C19 | C21 | C22 | 121.4(9) |
| N2 | Bi1 | Cl1 | 82.18(19) | C1 | C6 | C10 | 118.7(9) |
| N2 | Bi1 | Cl2 | 95.05(19) | C1 | C6 | C5 | 118.7(9) |
| C1 | Bi1 | Cl1 | 86.2(3) | C5 | C6 | C10 | 122.6(9) |
| C1 | Bi1 | Cl2 | 89.4(3) | C22 | C20 | C18 | 123.1(9) |
| C1 | Bi1 | N1 | 72.1(3) | C18 | C16 | C4 | 121.0(9) |
| C1 | Bi1 | N2 | 71.8(3) | C18 | C16 | C19 | 118.7(9) |
| C9 | N1 | Bi1 | 115.7(6) | C19 | C16 | C4 | 120.3(8) |
| C9 | N1 | C8 | 109.8(8) | C4 | C3 | C13 | 118.5(9) |
| C9 | N1 | C7 | 108.0(8) | C2 | C3 | C4 | 117.5(9) |
| C8 | N1 | Bi1 | 108.0(6) | C2 | C3 | C13 | 123.9(9) |
| C8 | N1 | C7 | 108.6(9) | C20 | C18 | C16 | 119.3(9) |
| C7 | N1 | Bi1 | 106.6(7) | C20 | C18 | C15 | 122.6(9) |
| C12 | N2 | Bi1 | 113.6(6) | C16 | C18 | C15 | 118.1(9) |
| C12 | N2 | C11 | 109.3(8) | C21 | C19 | C16 | 119.7(9) |
| C12 | N2 | C10 | 109.7(8) | C21 | C19 | C17 | 121.9(9) |
| C11 | N2 | Bi1 | 109.6(6) | C16 | C19 | C17 | 118.4(9) |
| C11 | N2 | C10 | 109.1(8) | C4 | C5 | C6 | 119.2(9) |
| C10 | N2 | Bi1 | 105.3(5) | C4 | C5 | C14 | 118.9(9) |
| C6 | C1 | Bi1 | 117.9(7) | C6 | C5 | C14 | 121.9(9) |
| C2 | C1 | Bi1 | 119.8(7) | C13 | C15 | C18 | 121.7(9) |
| C2 | C1 | C6 | 122.0(9) | C17 | C14 | C5 | 121.2(9) |
| C21 | C22 | C23 | 117.3(9) | C1 | C2 | C3 | 121.2(9) |
| C20 | C22 | C23 | 124.9(9) | C1 | C2 | C7 | 117.8(9) |
| C20 | C22 | C21 | 117.8(9) | C3 | C2 | C7 | 121.0(10) |
| C22 | C23 | C26 | 109.2(8) | C15 | C13 | C3 | 121.7(10) |
| C24 | C23 | C22 | 110.8(8) | C14 | C17 | C19 | 121.5(9) |
| C24 | C23 | C26 | 107.6(9) | C30 | C29 | C28 | 113.6(9) |

**Table S4.** Torsion Angles [°] for **1**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Bi1 | N1 | C7 | C2 | 39.9(10) | C6 | C1 | C2 | C7 | -179.5(10) |
| Bi1 | N2 | C10 | C6 | 39.2(9) | C6 | C5 | C14 | C17 | 178.0(10) |
| Bi1 | C1 | C6 | C10 | -5.3(12) | C20 | C22 | C23 | C26 | 119.2(11) |
| Bi1 | C1 | C6 | C5 | 172.4(7) | C20 | C22 | C23 | C24 | -122.5(11) |
| Bi1 | C1 | C2 | C3 | -173.7(8) | C20 | C22 | C23 | C25 | -0.4(15) |
| Bi1 | C1 | C2 | C7 | 6.6(13) | C20 | C22 | C21 | C19 | -1.1(15) |
| N2 | C10 | C6 | C1 | -26.3(13) | C20 | C18 | C15 | C13 | 179.5(11) |
| N2 | C10 | C6 | C5 | 156.1(9) | C16 | C4 | C3 | C2 | 177.7(9) |
| C1 | C6 | C5 | C4 | 2.1(14) | C16 | C4 | C3 | C13 | -3.9(15) |
| C1 | C6 | C5 | C14 | -176.5(10) | C16 | C4 | C5 | C6 | -179.1(9) |
| C1 | C2 | C7 | N1 | -33.6(14) | C16 | C4 | C5 | C14 | -0.5(14) |
| C12 | N2 | C10 | C6 | 161.8(8) | C16 | C18 | C15 | C13 | -1.1(16) |
| C9 | N1 | C7 | C2 | 164.8(9) | C16 | C19 | C17 | C14 | -0.7(16) |
| C11 | N2 | C10 | C6 | -78.4(10) | C3 | C4 | C16 | C18 | 2.4(15) |
| C22 | C21 | C19 | C16 | -0.4(15) | C3 | C4 | C16 | C19 | -177.2(9) |
| C22 | C21 | C19 | C17 | -179.0(10) | C3 | C4 | C5 | C6 | -1.1(15) |
| C22 | C20 | C18 | C16 | -0.6(16) | C3 | C4 | C5 | C14 | 177.6(10) |
| C22 | C20 | C18 | C15 | 178.7(10) | C3 | C2 | C7 | N1 | 146.7(10) |
| C23 | C22 | C21 | C19 | 177.2(9) | C18 | C16 | C19 | C21 | 1.4(15) |
| C23 | C22 | C20 | C18 | -176.5(10) | C18 | C16 | C19 | C17 | -179.9(9) |
| C10 | C6 | C5 | C4 | 179.6(9) | C18 | C15 | C13 | C3 | -0.4(18) |
| C10 | C6 | C5 | C14 | 1.1(16) | C19 | C16 | C18 | C20 | -1.0(15) |
| C4 | C16 | C18 | C20 | 179.5(9) | C19 | C16 | C18 | C15 | 179.7(10) |
| C4 | C16 | C18 | C15 | 0.1(15) | C5 | C4 | C16 | C18 | -179.5(9) |
| C4 | C16 | C19 | C21 | -179.0(9) | C5 | C4 | C16 | C19 | 0.9(15) |
| C4 | C16 | C19 | C17 | -0.4(15) | C5 | C4 | C3 | C2 | -0.3(15) |
| C4 | C3 | C2 | C1 | 0.8(16) | C5 | C4 | C3 | C13 | 178.1(10) |
| C4 | C3 | C2 | C7 | -179.5(10) | C5 | C14 | C17 | C19 | 1.1(17) |
| C4 | C3 | C13 | C15 | 2.9(17) | C8 | N1 | C7 | C2 | -76.3(11) |

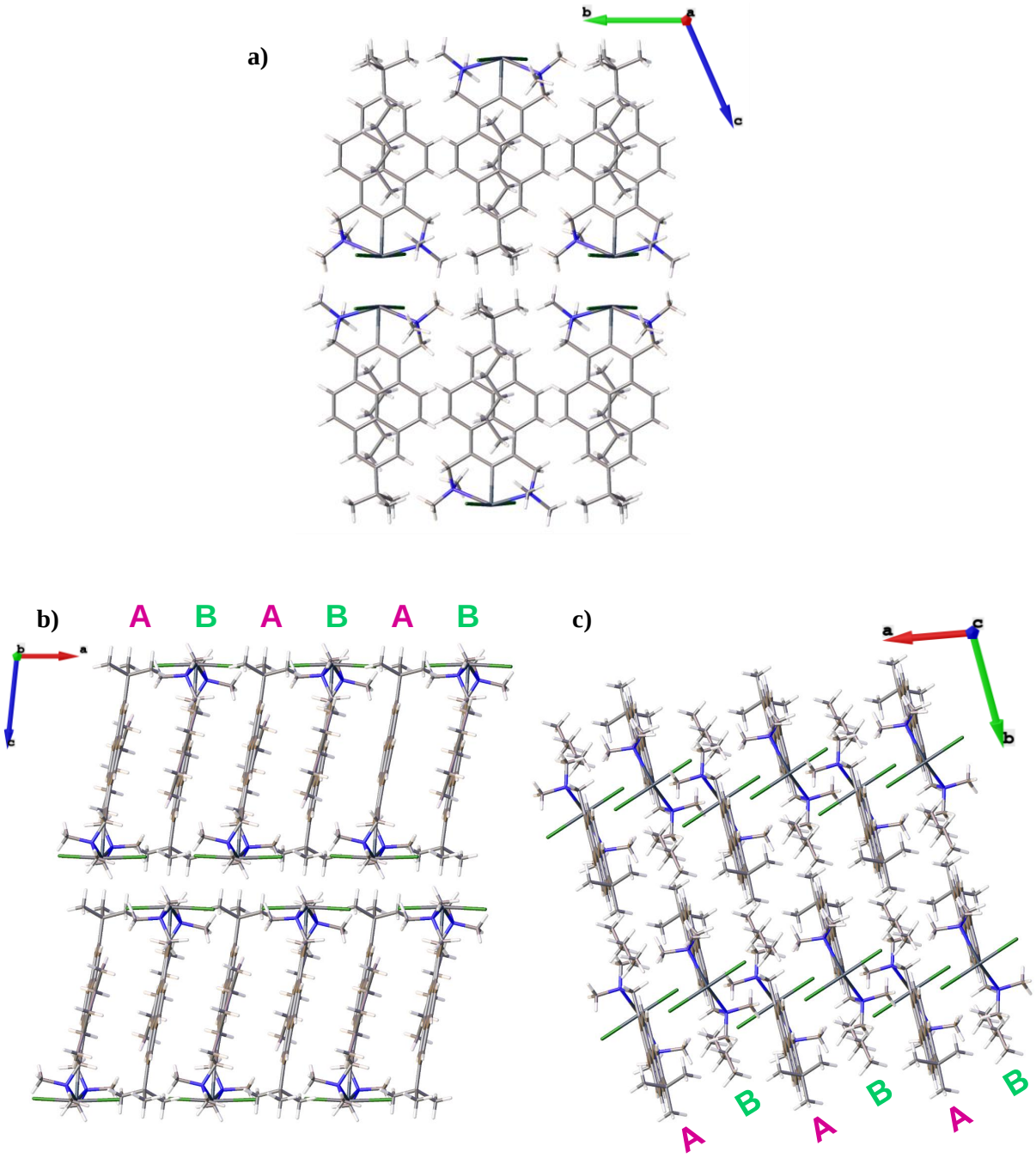



**Figure S11.** Packing diagrams of complex **1** viewed along (a) the *a*-axis, (b) the *b*-axis, and (c) the *c*-axis of the unit cell.

**Table S5.** Crystal data and structure refinement for **2**.

| | |
|---|---|
| Identification code | **2** |
| Empirical formula | $C_{45.5}H_{40}BiCl_3N_2$ |
| Formula weight | 930.12 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| $a$/Å | 14.0114(6) |
| $b$/Å | 20.1875(8) |
| $c$/Å | 15.1534(6) |
| $\alpha$/° | 90 |
| $\beta$/° | 114.972(3) |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 3885.5(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.590 |
| $\mu$/mm$^{-1}$ | 4.779 |
| $F$(000) | 1844.0 |
| Crystal size/mm$^3$ | 0.25 × 0.2 × 0.075 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.008 to 50.5 |
| Index ranges | $-16 \leq h \leq 16$, $-24 \leq k \leq 24$, $-18 \leq l \leq 18$ |
| Reflections collected | 16241 |
| Independent reflections | 7021 [$R_{int}$ = 0.0453, $R_{sigma}$ = 0.0569] |
| Data/restraints/parameters | 7021/36/482 |
| Goodness-of-fit on $F^2$ | 1.205 |
| Final R indexes [I ≥ 2σ (I)] | $R_1$ = 0.0815, w$R_2$ = 0.1939 |
| Final R indexes [all data] | $R_1$ = 0.1136, w$R_2$ = 0.2091 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.62/-1.93 |

**Table S6.** Bond Lengths [Å] for **2**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Bi1 | C13 | 2.334(14) | C24 | C23 | 1.45(2) |
| Bi1 | N2 | 2.793(14) | C2 | C1 | 1.40(2) |
| Bi1 | C29 | 2.275(16) | C2 | C7 | 1.52(2) |
| Bi1 | C1 | 2.270(14) | C2 | C3 | 1.39(2) |
| Cl4 | C46 | 1.73(2) | C34 | C35 | 1.37(2) |
| Cl3 | C46 | 1.78(2) | C34 | C33 | 1.40(3) |
| Cl1 | C45 | 1.77(4) | C19 | C18 | 1.42(2) |
| N1 | C8 | 1.45(2) | C19 | C20 | 1.42(3) |
| N1 | C9 | 1.44(2) | C14 | C15 | 1.42(2) |
| N1 | C7 | 1.49(2) | C25 | C26 | 1.48(2) |
| Cl2 | C45 | 1.75(4) | C40 | C41 | 1.35(2) |
| C13 | C14 | 1.34(2) | C40 | C39 | 1.45(2) |
| C13 | C26 | 1.43(2) | C43 | C44 | 1.44(2) |
| N2 | C10 | 1.50(2) | C22 | C23 | 1.36(2) |
| N2 | C12 | 1.45(2) | C22 | C21 | 1.42(2) |
| N2 | C11 | 1.45(3) | C1 | C6 | 1.41(2) |
| C42 | C29 | 1.43(2) | C10 | C6 | 1.53(2) |
| C42 | C43 | 1.41(2) | C18 | C17 | 1.33(2) |
| C42 | C41 | 1.44(2) | C6 | C5 | 1.37(2) |
| C28 | C27 | 1.40(2) | C4 | C5 | 1.38(2) |
| C28 | C19 | 1.43(2) | C4 | C3 | 1.36(2) |
| C28 | C23 | 1.44(2) | C35 | C36 | 1.42(2) |
| C27 | C26 | 1.38(2) | C35 | C44 | 1.44(2) |
| C27 | C16 | 1.42(2) | C36 | C37 | 1.37(3) |
| C29 | C30 | 1.39(2) | C15 | C16 | 1.39(2) |
| C32 | C31 | 1.46(2) | C39 | C44 | 1.44(2) |
| C32 | C43 | 1.38(2) | C39 | C38 | 1.33(2) |
| C32 | C33 | 1.41(2) | C17 | C16 | 1.44(2) |
| C31 | C30 | 1.33(2) | C38 | C37 | 1.36(2) |
| C24 | C25 | 1.34(2) | C21 | C20 | 1.38(3) |

**Table S7** Bond Angles [°] for **2**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C13 | Bi1 | N2 | 154.1(5) | C42 | C43 | C44 | 119.4(15) |
| C29 | Bi1 | C13 | 82.7(5) | C32 | C43 | C42 | 121.7(16) |
| C29 | Bi1 | N2 | 77.1(5) | C32 | C43 | C44 | 118.9(15) |
| C1 | Bi1 | C13 | 96.9(5) | C23 | C22 | C21 | 119.9(18) |
| C1 | Bi1 | N2 | 69.3(5) | C2 | C1 | Bi1 | 120.8(11) |
| C1 | Bi1 | C29 | 95.2(6) | C2 | C1 | C6 | 118.3(14) |
| C8 | N1 | C7 | 109.9(14) | C6 | C1 | Bi1 | 120.5(11) |
| C9 | N1 | C8 | 108.9(14) | C40 | C41 | C42 | 123.1(15) |
| C9 | N1 | C7 | 111.1(13) | N2 | C10 | C6 | 111.6(14) |
| C14 | C13 | Bi1 | 121.4(11) | C17 | C18 | C19 | 120.5(16) |
| C14 | C13 | C26 | 118.2(14) | C1 | C6 | C10 | 120.9(14) |
| C26 | C13 | Bi1 | 120.4(10) | C5 | C6 | C1 | 120.1(15) |
| C10 | N2 | Bi1 | 100.5(10) | C5 | C6 | C10 | 119.1(15) |
| C12 | N2 | Bi1 | 116.5(11) | C3 | C4 | C5 | 119.5(16) |
| C12 | N2 | C10 | 110.8(15) | C34 | C35 | C36 | 121.1(16) |
| C11 | N2 | Bi1 | 103.8(10) | C34 | C35 | C44 | 120.3(16) |
| C11 | N2 | C10 | 110.9(15) | C36 | C35 | C44 | 118.6(16) |
| C11 | N2 | C12 | 113.4(16) | C37 | C36 | C35 | 118.7(16) |
| C29 | C42 | C41 | 121.2(14) | C28 | C23 | C24 | 115.0(15) |
| C43 | C42 | C29 | 121.0(15) | C22 | C23 | C28 | 122.4(17) |
| C43 | C42 | C41 | 117.8(14) | C22 | C23 | C24 | 122.5(16) |
| C27 | C28 | C19 | 121.4(15) | C13 | C26 | C25 | 121.2(13) |
| C27 | C28 | C23 | 121.6(15) | C27 | C26 | C13 | 120.7(14) |
| C19 | C28 | C23 | 117.0(15) | C27 | C26 | C25 | 118.0(15) |
| C28 | C27 | C16 | 118.8(15) | C16 | C15 | C14 | 118.3(16) |
| C26 | C27 | C28 | 121.3(15) | C44 | C39 | C40 | 115.2(14) |
| C26 | C27 | C16 | 119.8(14) | C38 | C39 | C40 | 125.3(17) |
| C42 | C29 | Bi1 | 120.6(11) | C38 | C39 | C44 | 119.5(16) |
| C30 | C29 | Bi1 | 124.4(12) | C6 | C5 | C4 | 121.0(16) |
| C30 | C29 | C42 | 114.7(14) | C18 | C17 | C16 | 123.1(17) |
| C43 | C32 | C31 | 116.8(15) | C43 | C44 | C39 | 122.4(15) |
| C43 | C32 | C33 | 120.8(16) | C35 | C44 | C43 | 119.1(15) |
| C33 | C32 | C31 | 122.3(16) | C35 | C44 | C39 | 118.5(15) |
| C30 | C31 | C32 | 119.4(14) | C34 | C33 | C32 | 120.5(17) |
| C25 | C24 | C23 | 124.1(16) | C39 | C38 | C37 | 122.2(19) |
| C1 | C2 | C7 | 121.8(14) | C27 | C16 | C17 | 118.0(16) |
| C3 | C2 | C1 | 119.2(15) | C15 | C16 | C27 | 119.6(15) |
| C3 | C2 | C7 | 118.7(14) | C15 | C16 | C17 | 122.3(16) |
| C35 | C34 | C33 | 120.1(16) | C38 | C37 | C36 | 122.5(18) |
| C18 | C19 | C28 | 118.2(15) | N1 | C7 | C2 | 111.8(13) |
| C18 | C19 | C20 | 122.5(16) | C20 | C21 | C22 | 119.9(17) |
| C20 | C19 | C28 | 119.3(16) | C4 | C3 | C2 | 121.0(16) |

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C13 | C14 | C15 | 123.3(16) | C21 | C20 | C19 | 121.4(17) |
| C24 | C25 | C26 | 119.6(16) | Cl4 | C46 | Cl3 | 112.7(11) |
| C31 | C30 | C29 | 125.9(15) | Cl2 | C45 | Cl1 | 111(2) |
| C41 | C40 | C39 | 122.0(16) | | | | |

**Table S8.** Torsion Angles [°] for **2**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Bi1 | C13 | C14 | C15 | -179.0(12) | C43 | C32 | C31 | C30 | -7(2) |
| Bi1 | C13 | C26 | C27 | 179.3(11) | C43 | C32 | C33 | C34 | -6(2) |
| Bi1 | C13 | C26 | C25 | -3(2) | C22 | C21 | C20 | C19 | -1(3) |
| Bi1 | N2 | C10 | C6 | 41.8(15) | C1 | C2 | C7 | N1 | 39(2) |
| Bi1 | C29 | C30 | C31 | -175.1(12) | C1 | C2 | C3 | C4 | 3(2) |
| Bi1 | C1 | C6 | C10 | -1(2) | C1 | C6 | C5 | C4 | 3(3) |
| Bi1 | C1 | C6 | C5 | 178.4(13) | C41 | C42 | C29 | Bi1 | -8.0(19) |
| C13 | C14 | C15 | C16 | -1(3) | C41 | C42 | C29 | C30 | 178.1(14) |
| N2 | C10 | C6 | C1 | -34(2) | C41 | C42 | C43 | C32 | -178.1(14) |
| N2 | C10 | C6 | C5 | 146.2(16) | C41 | C42 | C43 | C44 | 3(2) |
| C8 | N1 | C7 | C2 | 64.8(17) | C41 | C40 | C39 | C44 | -1(2) |
| C42 | C29 | C30 | C31 | -1(2) | C41 | C40 | C39 | C38 | -178.1(16) |
| C42 | C43 | C44 | C35 | 176.4(14) | C10 | C6 | C5 | C4 | -177.5(16) |
| C42 | C43 | C44 | C39 | -4(2) | C18 | C19 | C20 | C21 | -179.4(16) |
| C28 | C27 | C26 | C13 | -174.9(15) | C18 | C17 | C16 | C27 | 2(3) |
| C28 | C27 | C26 | C25 | 7(2) | C18 | C17 | C16 | C15 | -178.0(17) |
| C28 | C27 | C16 | C15 | 177.5(15) | C35 | C34 | C33 | C32 | 6(3) |
| C28 | C27 | C16 | C17 | -2(2) | C35 | C36 | C37 | C38 | 2(3) |
| C28 | C19 | C18 | C17 | -2(2) | C36 | C35 | C44 | C43 | 178.7(14) |
| C28 | C19 | C20 | C21 | 0(3) | C36 | C35 | C44 | C39 | -1(2) |
| C27 | C28 | C19 | C18 | 1(2) | C23 | C28 | C27 | C26 | -4(2) |
| C27 | C28 | C19 | C20 | -178.5(15) | C23 | C28 | C27 | C16 | -179.3(15) |
| C27 | C28 | C23 | C24 | 0(2) | C23 | C28 | C19 | C18 | -178.5(15) |
| C27 | C28 | C23 | C22 | 177.1(17) | C23 | C28 | C19 | C20 | 2(2) |
| C29 | C42 | C43 | C32 | 5(2) | C23 | C24 | C25 | C26 | 3(3) |
| C29 | C42 | C43 | C44 | -174.2(14) | C23 | C22 | C21 | C20 | 0(3) |
| C29 | C42 | C41 | C40 | 175.7(15) | C26 | C13 | C14 | C15 | 3(2) |
| C32 | C31 | C30 | C29 | 7(2) | C26 | C27 | C16 | C15 | 2(2) |
| C32 | C43 | C44 | C35 | -2(2) | C26 | C27 | C16 | C17 | -177.9(15) |
| C32 | C43 | C44 | C39 | 177.5(14) | C39 | C40 | C41 | C42 | 1(2) |
| C31 | C32 | C43 | C42 | 1(2) | C39 | C38 | C37 | C36 | -4(3) |
| C31 | C32 | C43 | C44 | -180.0(13) | C5 | C4 | C3 | C2 | -9(3) |
| C31 | C32 | C33 | C34 | 178.5(15) | C44 | C35 | C36 | C37 | 0(2) |

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C24 | C25 | C26 | C13 | 175.6(15) | C44 | C39 | C38 | C37 | 3(2) |
| C24 | C25 | C26 | C27 | -7(2) | C33 | C32 | C31 | C30 | 168.3(15) |
| C2 | C1 | C6 | C10 | 172.0(15) | C33 | C32 | C43 | C42 | -174.1(15) |
| C2 | C1 | C6 | C5 | -8(2) | C33 | C32 | C43 | C44 | 5(2) |
| C34 | C35 | C36 | C37 | 177.2(16) | C33 | C34 | C35 | C36 | 179.7(16) |
| C34 | C35 | C44 | C43 | 2(2) | C33 | C34 | C35 | C44 | -3(2) |
| C34 | C35 | C44 | C39 | -178.1(14) | C38 | C39 | C44 | C43 | 179.9(15) |
| C19 | C28 | C27 | C26 | 176.3(15) | C38 | C39 | C44 | C35 | 0(2) |
| C19 | C28 | C27 | C16 | 1(2) | C12 | N2 | C10 | C6 | 165.6(15) |
| C19 | C28 | C23 | C24 | 179.5(14) | C16 | C27 | C26 | C13 | 0(2) |
| C19 | C28 | C23 | C22 | -3(2) | C16 | C27 | C26 | C25 | -177.4(14) |
| C19 | C18 | C17 | C16 | 0(3) | C9 | N1 | C7 | C2 | -174.6(13) |
| C14 | C13 | C26 | C27 | -3(2) | C7 | C2 | C1 | Bi1 | 3.8(19) |
| C14 | C13 | C26 | C25 | 174.6(15) | C7 | C2 | C1 | C6 | -169.4(14) |
| C14 | C15 | C16 | C27 | -2(2) | C7 | C2 | C3 | C4 | 178.3(15) |
| C14 | C15 | C16 | C17 | 178.2(16) | C21 | C22 | C23 | C28 | 2(3) |
| C25 | C24 | C23 | C28 | 1(3) | C21 | C22 | C23 | C24 | 179.6(17) |
| C25 | C24 | C23 | C22 | -176.5(18) | C11 | N2 | C10 | C6 | -67.5(18) |
| C40 | C39 | C44 | C43 | 2(2) | C3 | C2 | C1 | Bi1 | 178.4(11) |
| C40 | C39 | C44 | C35 | -177.8(13) | C3 | C2 | C1 | C6 | 5(2) |
| C40 | C39 | C38 | C37 | 179.8(16) | C3 | C2 | C7 | N1 | -136.1(14) |
| C43 | C42 | C29 | Bi1 | 169.4(11) | C3 | C4 | C5 | C6 | 6(3) |
| C43 | C42 | C29 | C30 | -5(2) | C20 | C19 | C18 | C17 | 177.9(17) |
| C43 | C42 | C41 | C40 | -2(2) | | | | | |

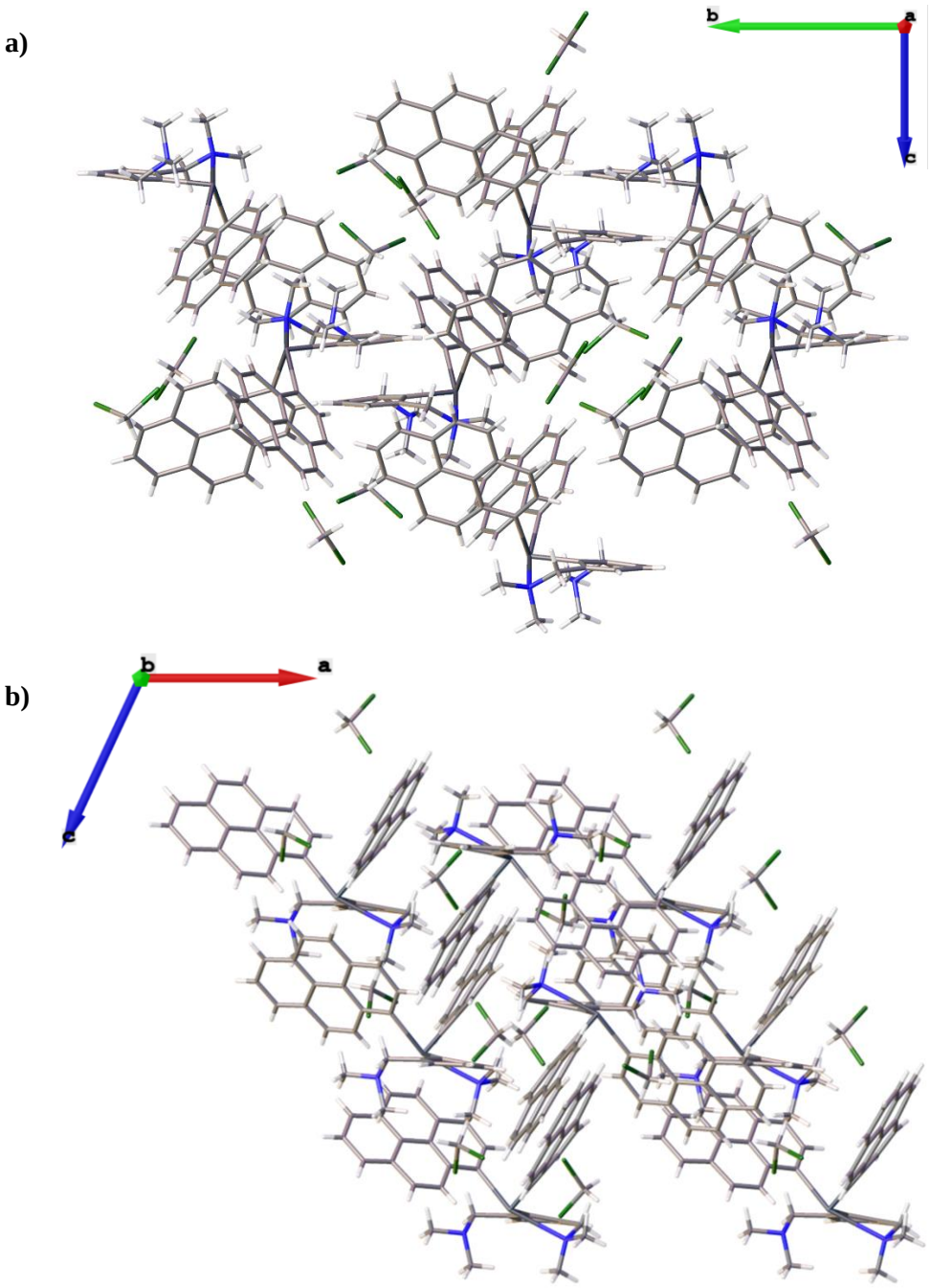



**Figure S12.** Packing diagrams of complex **2** viewed along (a) the *a*-axis and (b) the *b*-axis of the unit cell.

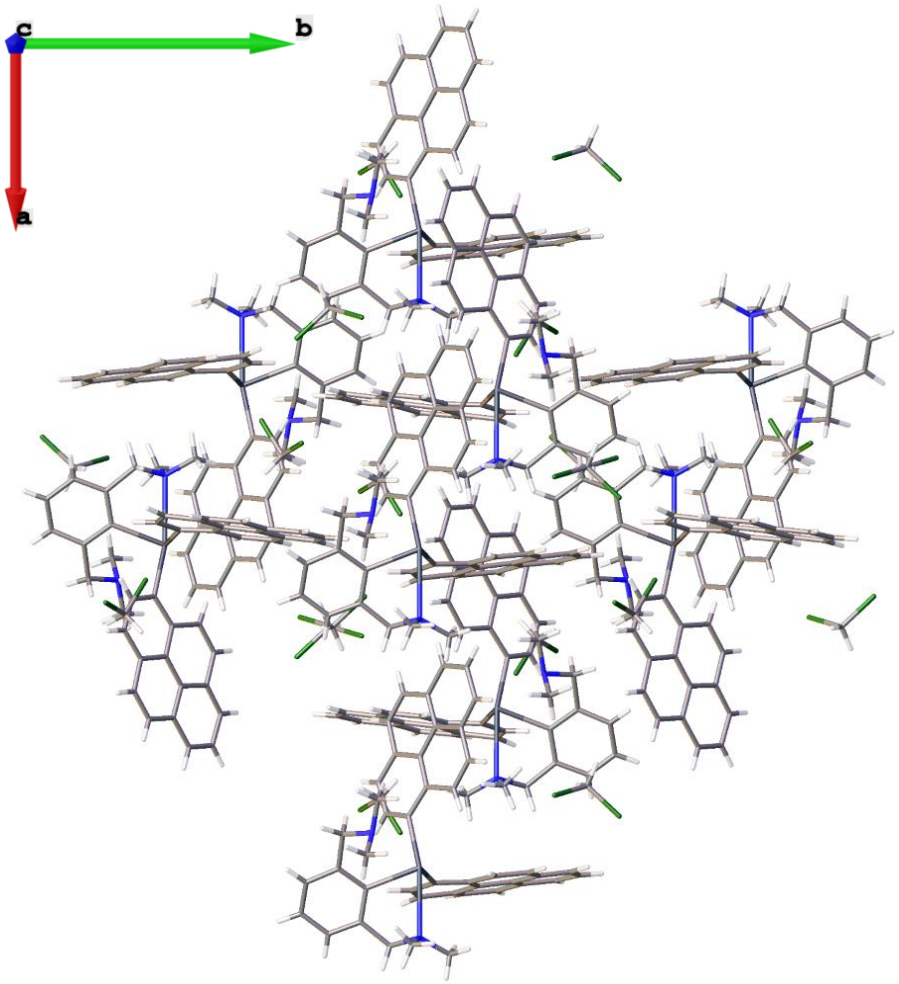



**Figure S13.** Packing diagrams of complex **2** viewed along the *c*-axis of the unit cell.

## UV/Vis Spectroscopy

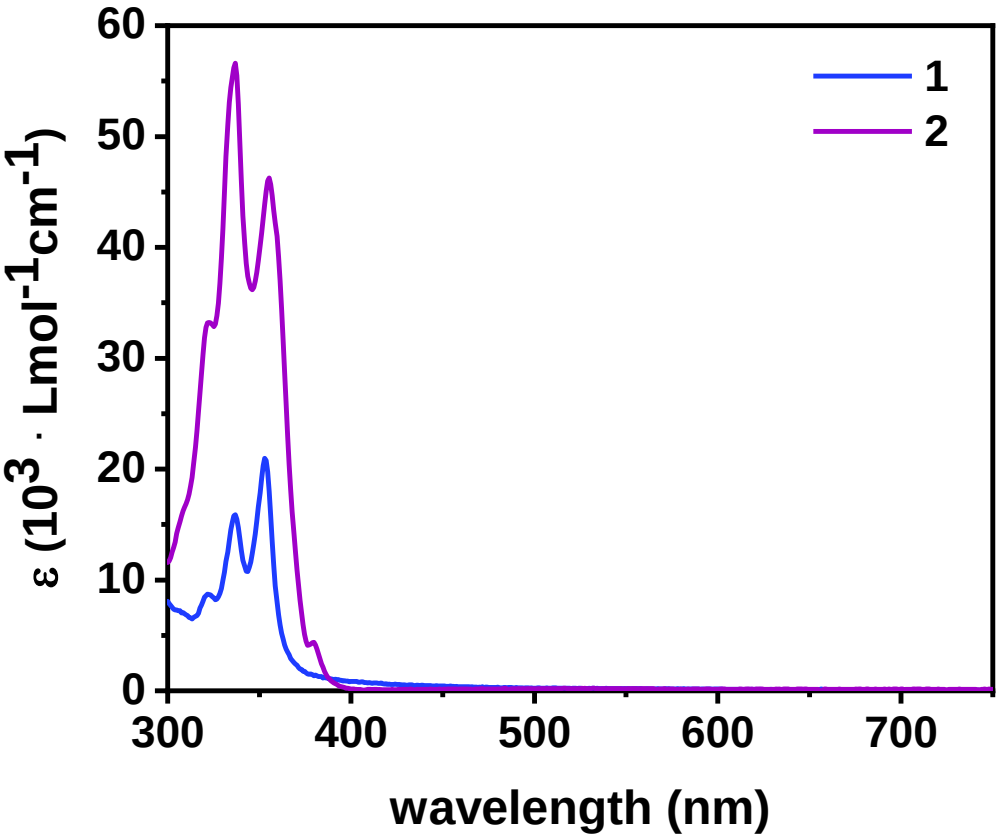



**Figure S14.** UV/Vis absorption spectra of **1** (top) and **2** (bottom) in $CH_2Cl_2$.

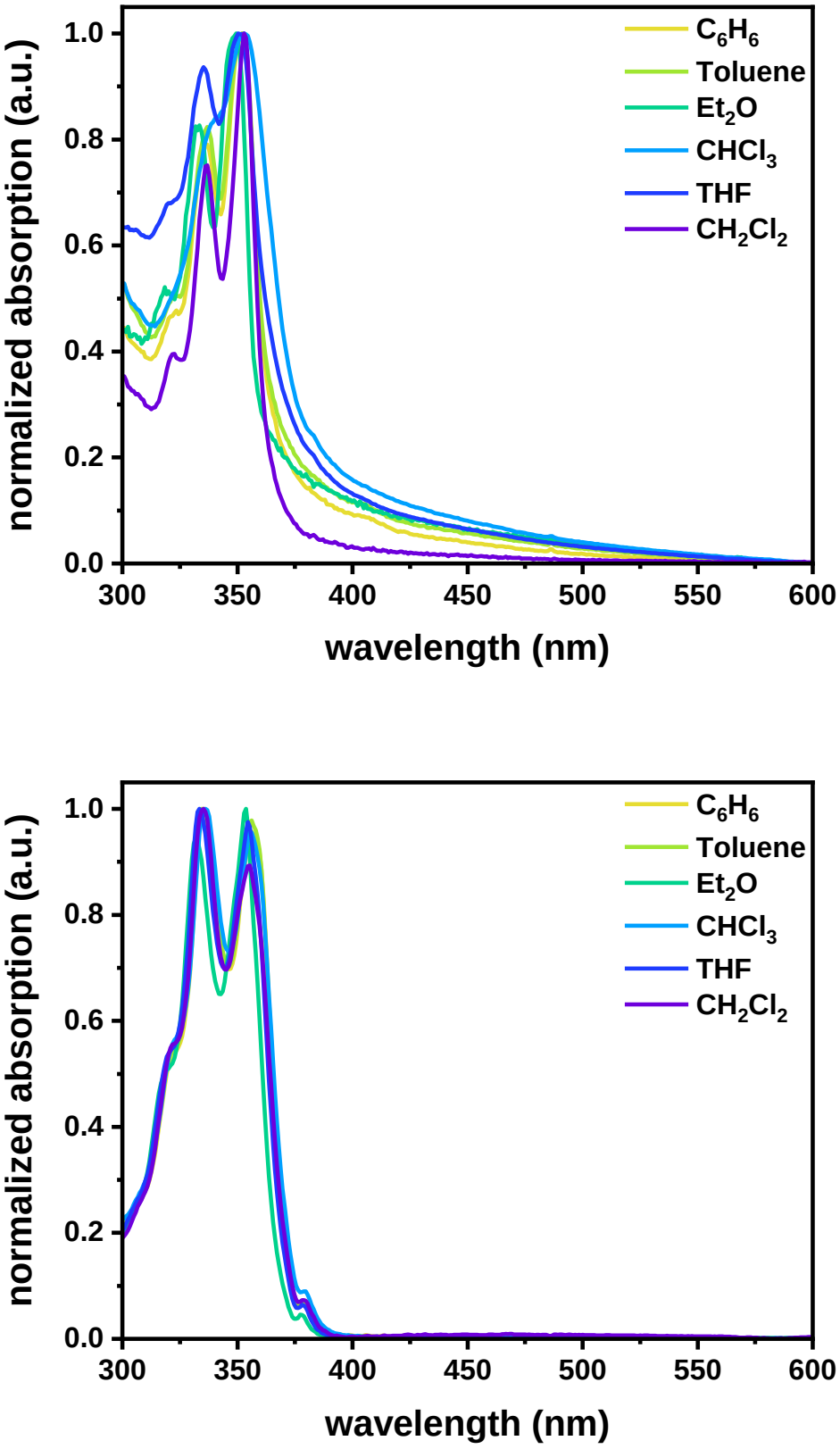



**Figure S15.** UV/Vis absorption spectra of **1** (top) and **2** (bottom) in different solvents.

## TD-DFT Data

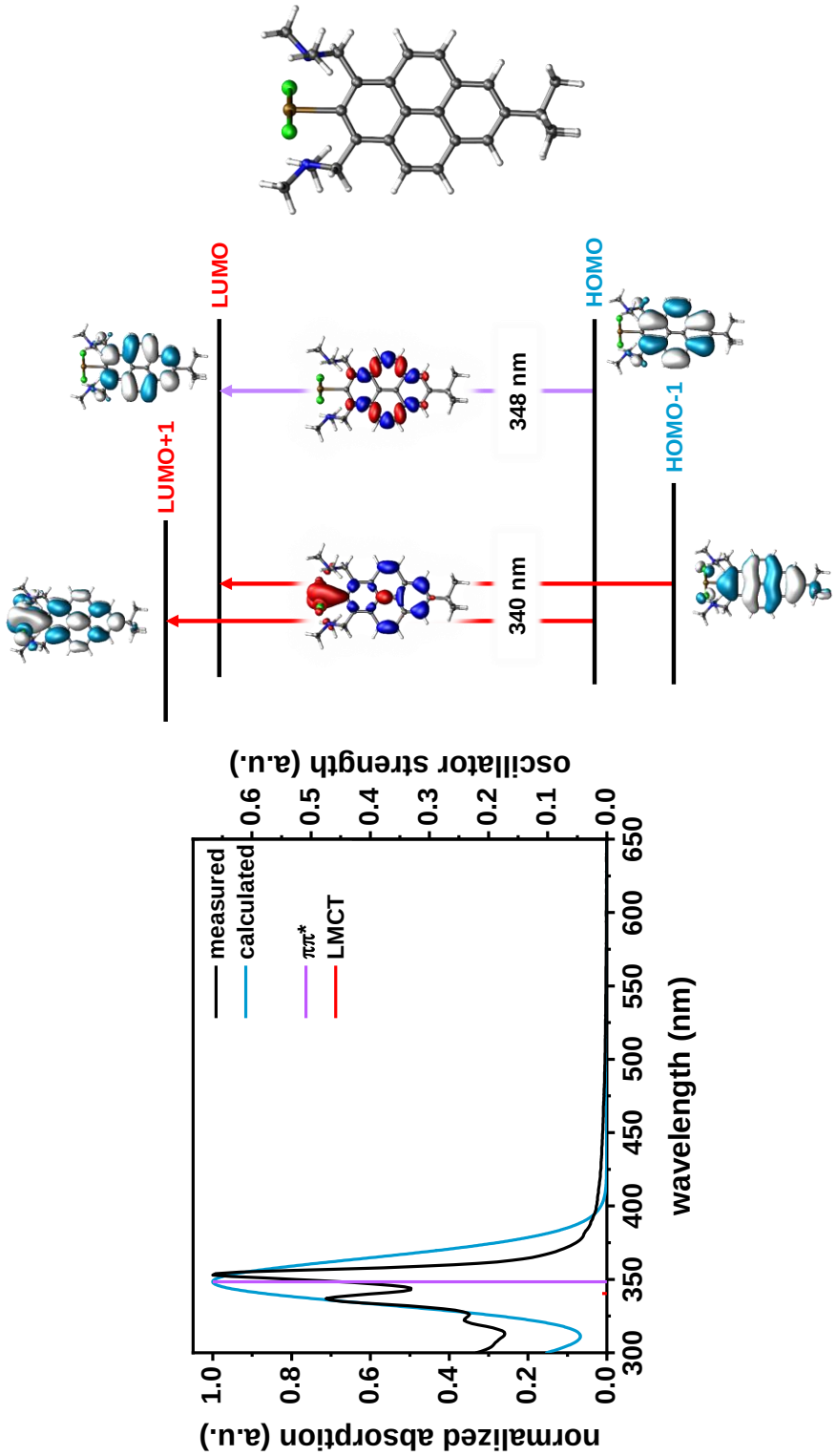



**Figure S16.** Top: Geometry-optimized structure of complex **1**. Middle: MO diagrams of relevant molecular orbitals involved in the individual TD-DFT computed electronic transitions along with the corresponding electron density difference maps. A loss of electron density is indicated in blue, a gain in red colour. Bottom: Comparison between the experimental (black line) and the TD-DFT computed (blue line) electronic absorption spectra. Individual electronic transitions are indicated as coloured bars.

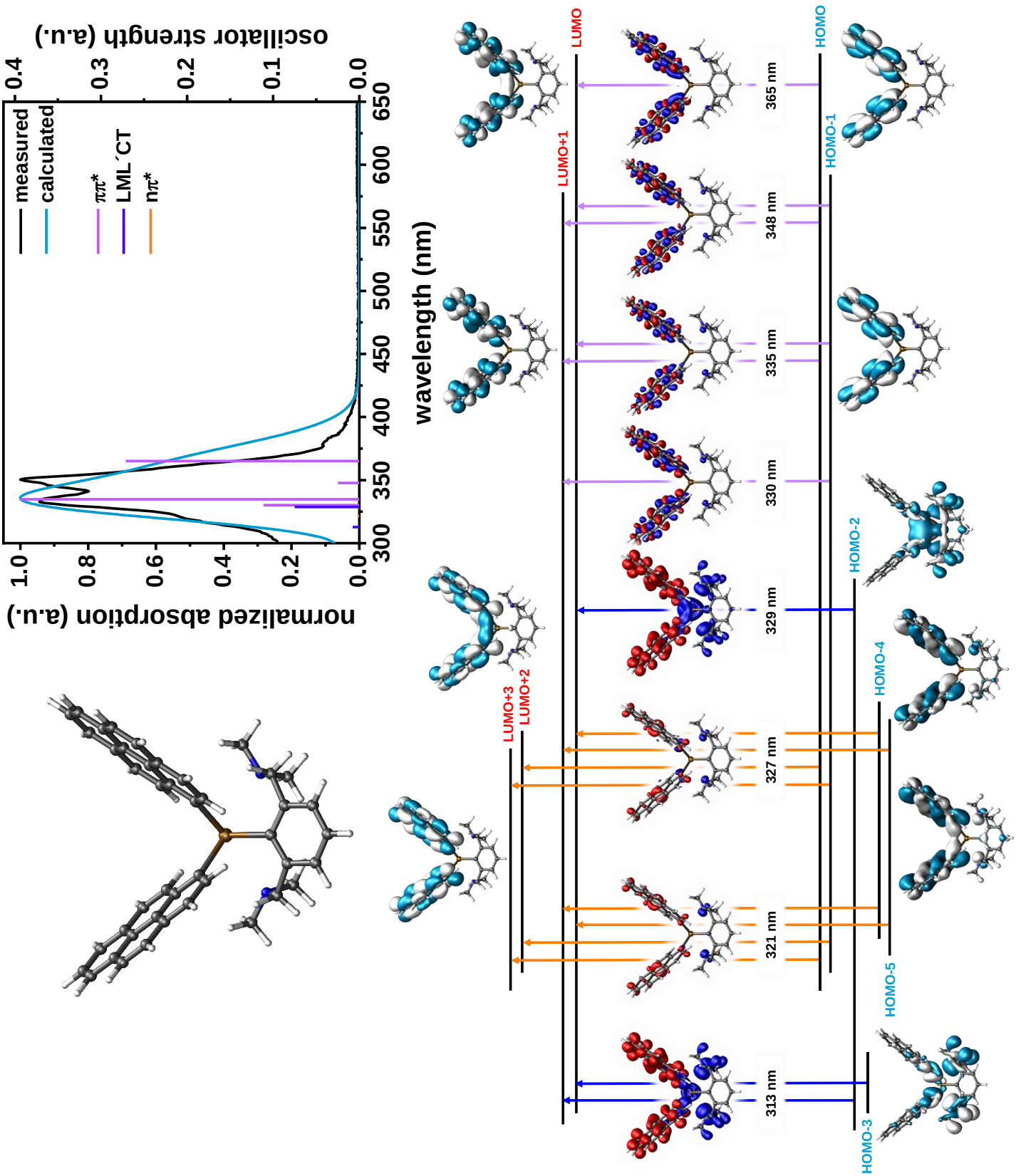



**Figure S17.** Left: Geometry-optimized structure of complex **2** along with comparison between the experimental (black line) and the TD-DFT computed (blue line) electronic absorption spectra. Individual electronic transitions are indicated as coloured bars. Right: MO diagrams of relevant molecular orbitals involved in the individual TD-DFT computed electronic transitions along with the corresponding electron density difference maps. A loss of electron density is indicated in blue, a gain in red colour.

**Table S9.** XYZ coordinates of the DFT-optimized structure of complex **1**.

| Atom | X | Y | Z |
|---|---|---|---|
| Bi | -3.20610 | -0.00533 | 0.00033 |
| C | -0.99396 | 0.00312 | 0.00026 |
| N | -2.45052 | 2.36191 | 0.48413 |
| C | -3.41620 | 3.35122 | -0.00935 |
| H | -3.61380 | 3.17051 | -1.06884 |
| H | -3.03058 | 4.37225 | 0.12054 |
| H | -4.34965 | 3.25588 | 0.55196 |
| N | -2.43252 | -2.36638 | -0.48457 |
| C | -2.23104 | 2.54382 | 1.92571 |
| H | -3.16830 | 2.38953 | 2.46455 |
| H | -1.85963 | 3.55888 | 2.12748 |
| H | -1.50097 | 1.81481 | 2.28289 |
| C | -1.17142 | 2.47309 | -0.24382 |
| H | -0.64555 | 3.37066 | 0.10654 |
| H | -1.41094 | 2.62231 | -1.30357 |
| C | -2.21066 | -2.54623 | -1.92600 |
| H | -3.14858 | -2.39831 | -2.46547 |
| H | -1.83193 | -3.55859 | -2.12777 |
| H | -1.48545 | -1.81203 | -2.28242 |
| C | -1.15325 | -2.46839 | 0.24452 |
| H | -1.39288 | -2.61788 | 1.30421 |
| H | -0.62132 | -3.36295 | -0.10434 |
| C | -3.39151 | -3.36274 | 0.00774 |
| H | -3.59098 | -3.18415 | 1.06724 |
| H | -2.99873 | -4.38097 | -0.12262 |
| H | -4.32529 | -3.27350 | -0.55406 |
| Cl | -3.19769 | -0.75599 | 2.59053 |
| Cl | -3.20358 | 0.74516 | -2.58979 |
| C | 6.06244 | 0.03149 | -0.00231 |
| C | 5.33606 | 1.21564 | -0.13150 |
| C | 3.93364 | 1.23408 | -0.13267 |
| C | 3.21153 | 0.01841 | -0.00127 |
| C | 3.94377 | -1.19417 | 0.12988 |
| C | 5.34122 | -1.16157 | 0.12755 |
| C | 3.19659 | 2.45280 | -0.26590 |
| C | 1.78562 | 0.01300 | -0.00080 |
| C | 1.07751 | 1.24889 | -0.11766 |
| C | 1.83748 | 2.45928 | -0.25870 |
| C | -0.33219 | 1.22446 | -0.09592 |
| C | -0.32229 | -1.21426 | 0.09589 |
| C | 1.08633 | -1.22818 | 0.11641 |
| C | 1.85594 | -2.43406 | 0.25691 |
| C | 3.21406 | -2.41888 | 0.26346 |
| H | 3.77100 | -3.34643 | 0.37205 |
| H | 1.34215 | -3.38269 | 0.37092 |
| H | 3.74716 | 3.38412 | -0.37483 |
| H | 5.85152 | 2.16547 | -0.23537 |
| H | 5.87012 | -2.10628 | 0.23092 |
| H | 1.31737 | 3.40448 | -0.37254 |
| C | 7.59261 | -0.00338 | 0.00052 |
| C | 8.08530 | -0.61221 | 1.32366 |
| C | 8.08238 | -0.86850 | -1.17243 |
| C | 8.20662 | 1.39168 | -0.14307 |
| H | 7.75419 | -0.01139 | 2.17840 |
| H | 7.71639 | -1.63361 | 1.46561 |
| H | 9.18130 | -0.64817 | 1.33614 |
| H | 7.75212 | -0.45175 | -2.13079 |
| H | 9.17826 | -0.90984 | -1.17790 |
| H | 7.70951 | -1.89606 | -1.10458 |
| H | 9.29931 | 1.31130 | -0.13419 |
| H | 7.91758 | 1.86972 | -1.08615 |
| H | 7.91636 | 2.05201 | 0.68230 |

**Table S10.** XYZ coordinates of the DFT-optimized structure of complex **2**.

| Atom | X | Y | Z |
|---|---|---|---|
| Bi | 0.00450 | -1.29574 | -0.74442 |
| N | -2.49407 | -2.90117 | -0.98931 |
| C | -1.54562 | -0.09393 | 0.47048 |
| N | 2.50498 | -2.88163 | -1.02409 |
| C | -2.25595 | -4.04321 | -1.85690 |
| H | -3.06627 | -4.79222 | -1.79191 |
| H | -1.31561 | -4.53164 | -1.58573 |
| H | -2.18313 | -3.70390 | -2.89527 |
| C | 2.28091 | 0.96577 | -0.13923 |
| C | -3.93040 | 2.79769 | 0.05465 |
| C | -3.17669 | 1.74586 | 0.65392 |
| C | 1.55598 | -0.08751 | 0.46175 |
| C | 3.32649 | 1.50151 | 2.03573 |
| C | 2.60019 | 0.44885 | 2.60447 |
| H | 2.71645 | 0.23622 | 3.66537 |
| C | -2.92679 | 2.24132 | -2.11326 |
| H | -2.84071 | 2.43641 | -3.17973 |
| C | -1.18985 | -3.78019 | 0.91351 |
| C | 4.91818 | 3.33223 | 2.23726 |
| H | 5.59244 | 3.94222 | 2.83377 |
| C | -4.80913 | 3.59304 | 0.84714 |
| C | -1.70400 | -0.30795 | 1.84387 |
| H | -1.14537 | -1.10472 | 2.33104 |
| C | -2.21016 | 1.23928 | -1.53921 |
| H | -1.55647 | 0.63173 | -2.16079 |
| C | 1.73625 | -0.31753 | 1.82984 |
| H | 1.19384 | -1.12720 | 2.31410 |
| C | 2.87350 | 2.29738 | -2.10989 |
| H | 2.76927 | 2.50612 | -3.17214 |
| C | 3.16940 | 1.76754 | 0.64634 |
| C | -4.56003 | 4.09909 | -1.90954 |
| H | -4.46579 | 4.29642 | -2.97473 |
| C | 0.01785 | -3.15012 | 0.55701 |
| C | 2.17600 | 1.28008 | -1.53911 |
| H | 1.51906 | 0.67460 | -2.15926 |
| C | 2.56407 | -3.27262 | 0.37924 |
| H | 2.88278 | -2.39133 | 0.94800 |
| H | 3.33107 | -4.05281 | 0.54300 |
| C | -4.91891 | 3.31319 | 2.24925 |
| H | -5.59091 | 3.92405 | 2.84743 |
| C | 1.23396 | -3.77442 | 0.89485 |
| C | 0.03552 | -5.48489 | 2.12720 |
| H | 0.04240 | -6.37873 | 2.74533 |
| C | 4.78514 | 3.62926 | 0.84071 |
| C | 5.49502 | 4.67352 | 0.23252 |
| H | 6.16650 | 5.27817 | 0.83753 |
| C | -3.81155 | 3.06049 | -1.33971 |
| C | -2.29089 | 0.94319 | -0.13373 |
| C | -2.56545 | 0.45908 | 2.62063 |
| H | -2.66444 | 0.25921 | 3.68575 |
| C | 3.76123 | 3.11525 | -1.33840 |
| C | 1.22980 | -4.92534 | 1.68942 |
| H | 2.17627 | -5.39753 | 1.94530 |
| C | -4.20276 | 2.31038 | 2.82201 |
| H | -4.29318 | 2.10664 | 3.88652 |
| C | 3.90324 | 2.83520 | 0.05041 |
| C | 4.22079 | 2.31454 | 2.80688 |
| H | 4.32870 | 2.09780 | 3.86718 |
| C | 4.49051 | 4.16916 | -1.90504 |
| H | 4.37863 | 4.37963 | -2.96600 |
| C | 3.71988 | -2.19052 | -1.42159 |
| H | 3.62779 | -1.85463 | -2.45959 |
| H | 4.61268 | -2.83781 | -1.34691 |
| H | 3.87046 | -1.31262 | -0.78738 |
| C | -3.31106 | 1.49650 | 2.04875 |

| | | | |
|---|---|---|---|
| C | 5.34747 | 4.93888 | -1.12516 |
| H | 5.90570 | 5.75303 | -1.57940 |
| C | -3.72087 | -2.22241 | -1.37143 |
| H | -3.64789 | -1.89093 | -2.41235 |
| H | -3.86932 | -1.34269 | -0.73928 |
| H | -4.60672 | -2.87705 | -1.27967 |
| C | -2.52965 | -3.28550 | 0.41680 |
| H | -3.29107 | -4.06773 | 0.59613 |
| H | -2.84278 | -2.40260 | 0.98615 |
| C | -5.41358 | 4.87038 | -1.12745 |
| H | -5.98681 | 5.67260 | -1.58424 |
| C | 2.26193 | -4.02079 | -1.89404 |
| H | 1.32974 | -4.51787 | -1.61069 |
| H | 3.07887 | -4.76381 | -1.84593 |
| H | 2.16996 | -3.67652 | -2.92926 |
| C | -1.16803 | -4.93091 | 1.70804 |
| H | -2.10821 | -5.40754 | 1.97847 |
| C | -5.53867 | 4.62173 | 0.23562 |
| H | -6.20759 | 5.22751 | 0.84233 |

# Photoluminescence Data

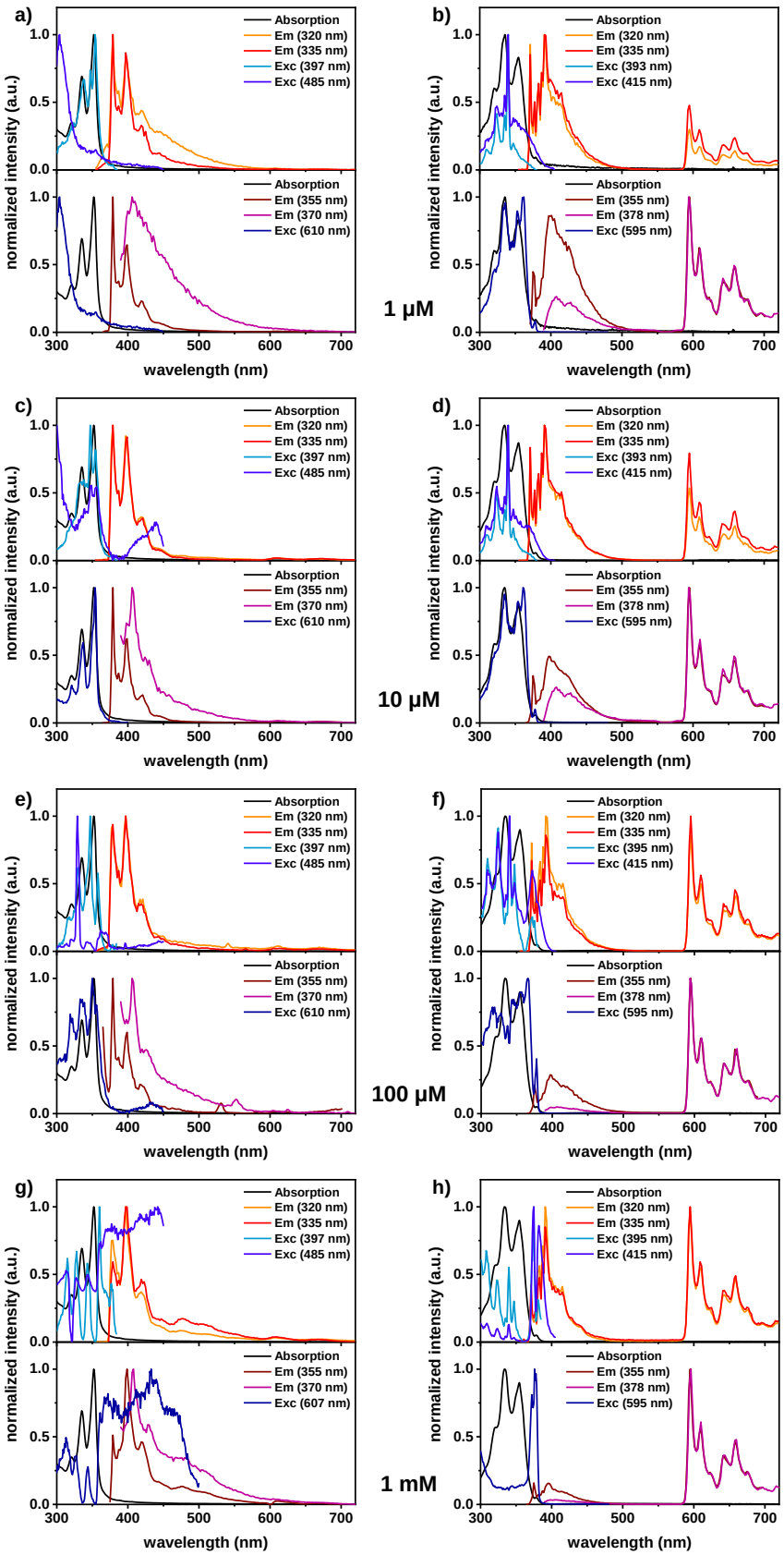



**Figure S18.** PL data at 77 K in MeTHF of (a) **1** at *c* = 1 µM. (b) **2** at *c* = 1 µM. (c) **1** at *c* = 10 µM. (d) **2** at *c* = 10 µM. (e) **1** at *c* = 100 µM. (f) **2** at *c* = 100 µM. (g) **1** at *c* = 1 mM. (h) **2** at *c* = 1 mM. Absorption spectra are depicted as black, emission spectra as red and excitation spectra as blue lines.

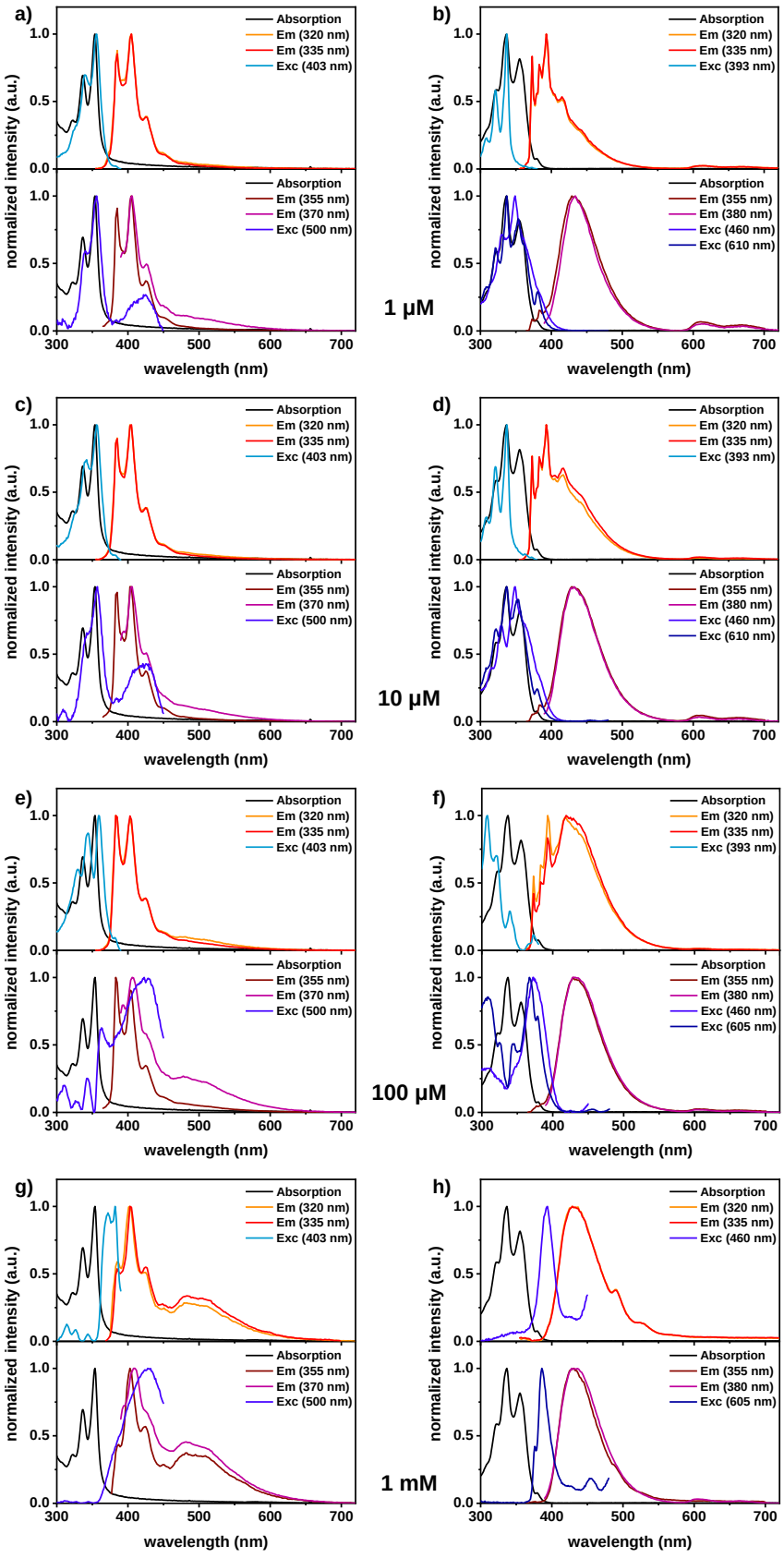



**Figure S19.** PL data at r.t. in degassed $CH_2Cl_2$ of (a) **1** at $c$ = 1 µM. (b) **2** at $c$ = 1 µM. (c) **1** at $c$ = 10 µM. (d) **2** at $c$ = 10 µM. (e) **1** at $c$ = 100 µM. (f) **2** at $c$ = 100 µM. (g) **1** at $c$ = 1 mM. (h) **2** at $c$ = 1 mM. Absorption spectra are depicted as black, emission spectra as red and excitation spectra as blue lines.

**Table S11.** Photoluminescence and absorption data for complexes **1** and **2**.

| | $\lambda_{max}$ (nm), [$\varepsilon\lambda$] ($\times 10^{-3} \cdot M^{-1} cm^{-1}$)[b] | $\lambda_{Em}$ (nm) | $\lambda_{Exc}$ (nm) | $\tau_F$ (ns)[c] | $\tau_P$ (ms)[c] |
|---|---|---|---|---|---|
| **1** | 322 [8.4]<br>337 [15.8]<br>354 [20.9] | **F**: 379, 387, 397, 421[a] | 335 , 347, 354[a] | 20 [40%], 170 [60%][a] | - |
| | | [a]**P**: 610, 675[a] | 321, 337, 354 [a] | - | 2.0 [97%], 10 [3%][a] |
| | | **F**: 385, 405,425, 451[b] | 326, 341, 356 [b] | 17 [15%], 59 [85%][b] | - |
| **2** | 322 [31.6]<br>337 [56.6]<br>355 [50.6]<br>380 [4.5] | **F**: 371, 377, 383, 387, 391, 415[a] | 310, 323, 335, 340, 347[a] | 2.3 [95%], 13 [4%], 150 [1%] [a] | - |
| | | **P**: 595, 610, 642, 658[a] | 321, 335, 354 , 361, 378[a] | - | 4.6 [100%] [a] |
| | | **F**: 373, 383, 393, 417[b] | 308, 321 ,337, 363[b] | 2.5 [84%], 20 [13%], 132 [3%][b] | - |
| | | [b]**Excimer**: 432[b] | 394[b] | 2.5 [100%] | - |
| | | [b]**P**: 610, 665[b] | 322, 337, 353, 380[b] | - | 0.10 [58%], 0.21 [42%][b] |

*[a] In MeTHF at 77 K; [b] in $CH_2Cl_2$ at r.t., [c] relative contributions in [%].*

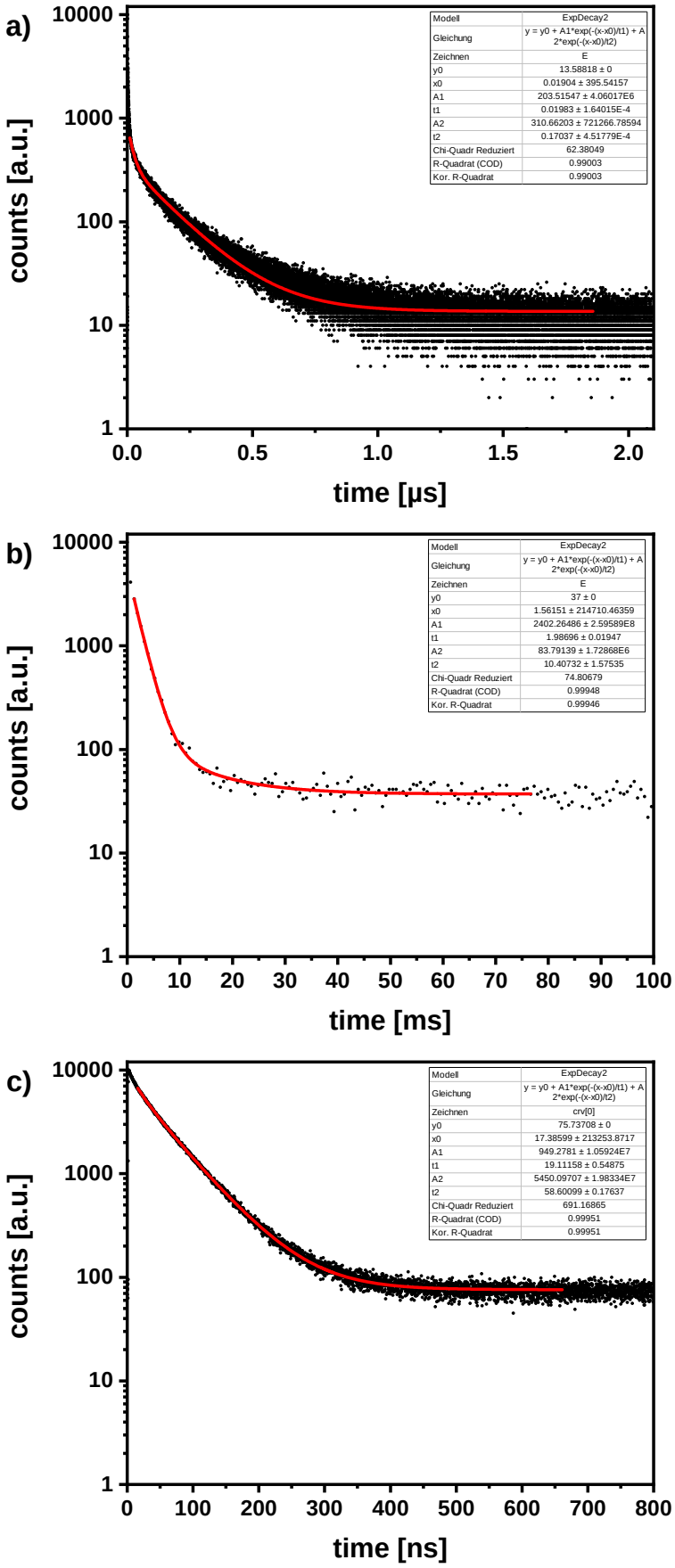



**Figure S20.** Lifetime measurements of (a) the 397 nm emission of **1** at 77 K in MeTHF; (b) the 610 nm emission of **1** at 77 K in MeTHF; (c) the 403 nm emission of **1** in degassed $CH_2Cl_2$ at r.t..

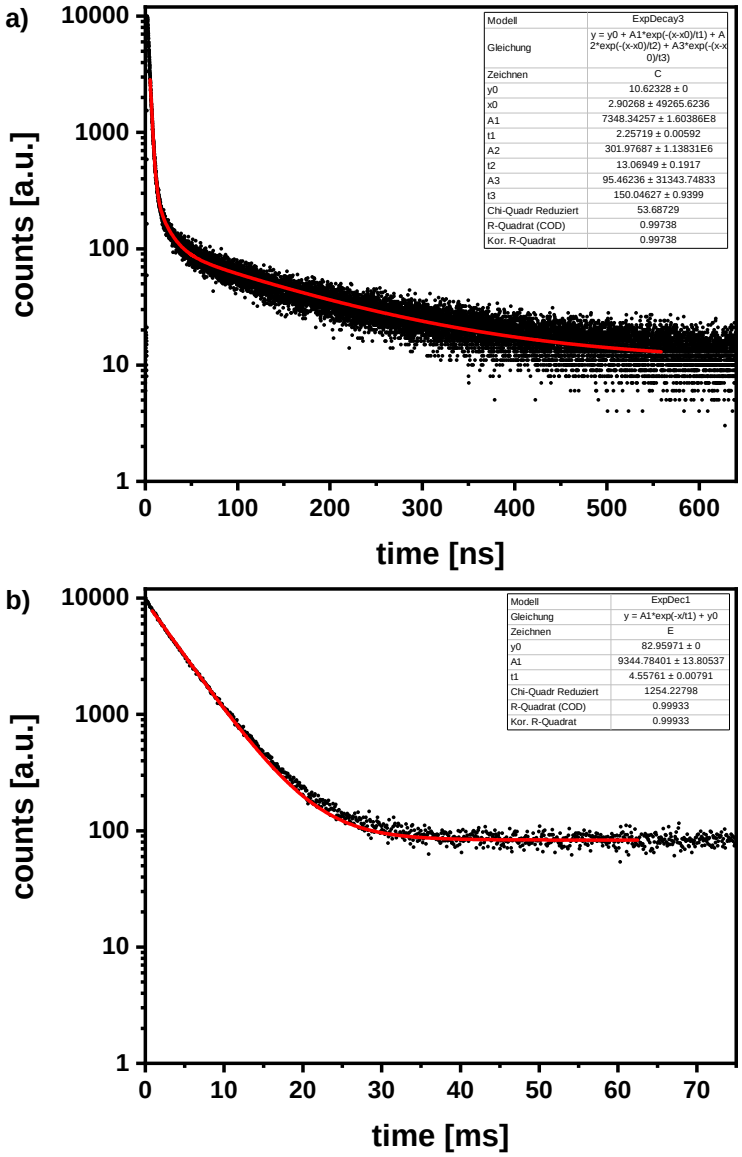



**Figure S21.** Lifetime measurements of (a) the 393 nm emission of **2** at 77 K in MeTHF; (b) the 595 nm emission of **2** at 77 K in MeTHF.

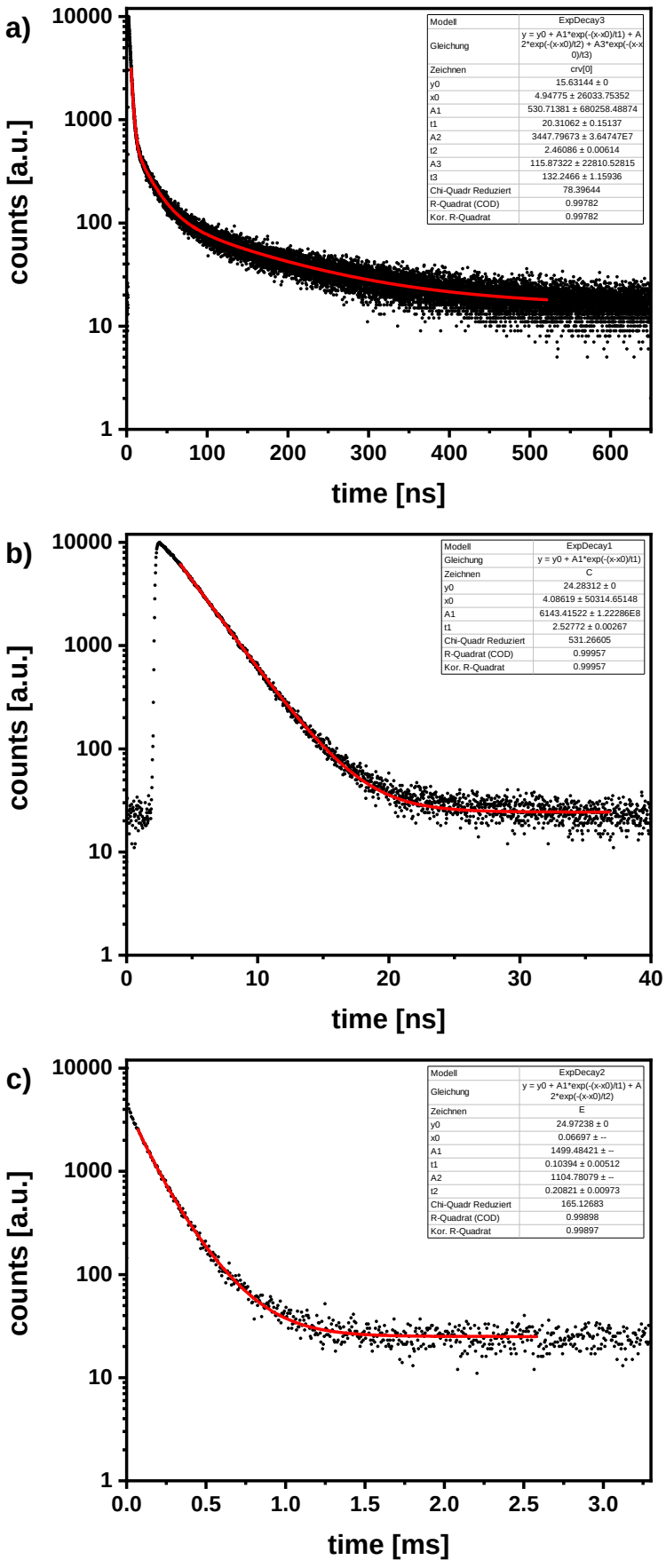



**Figure S22.** Lifetime measurements of (a) the 393 nm emission of **2** at r.t. in degassed $CH_2Cl_2$; (b) the 430 nm emission of **2** at r.t. in degassed $CH_2Cl_2$; (c) the 610 nm emission of **2** at r.t. in degassed $CH_2Cl_2$.

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