Electronic Supplementary Information for:

Tuning the Au–Au interactions by varying the degree of polymerisation in linear polymeric Au(I) *N*-heterocyclic carbene complexes

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1. TG/DTA Analysis

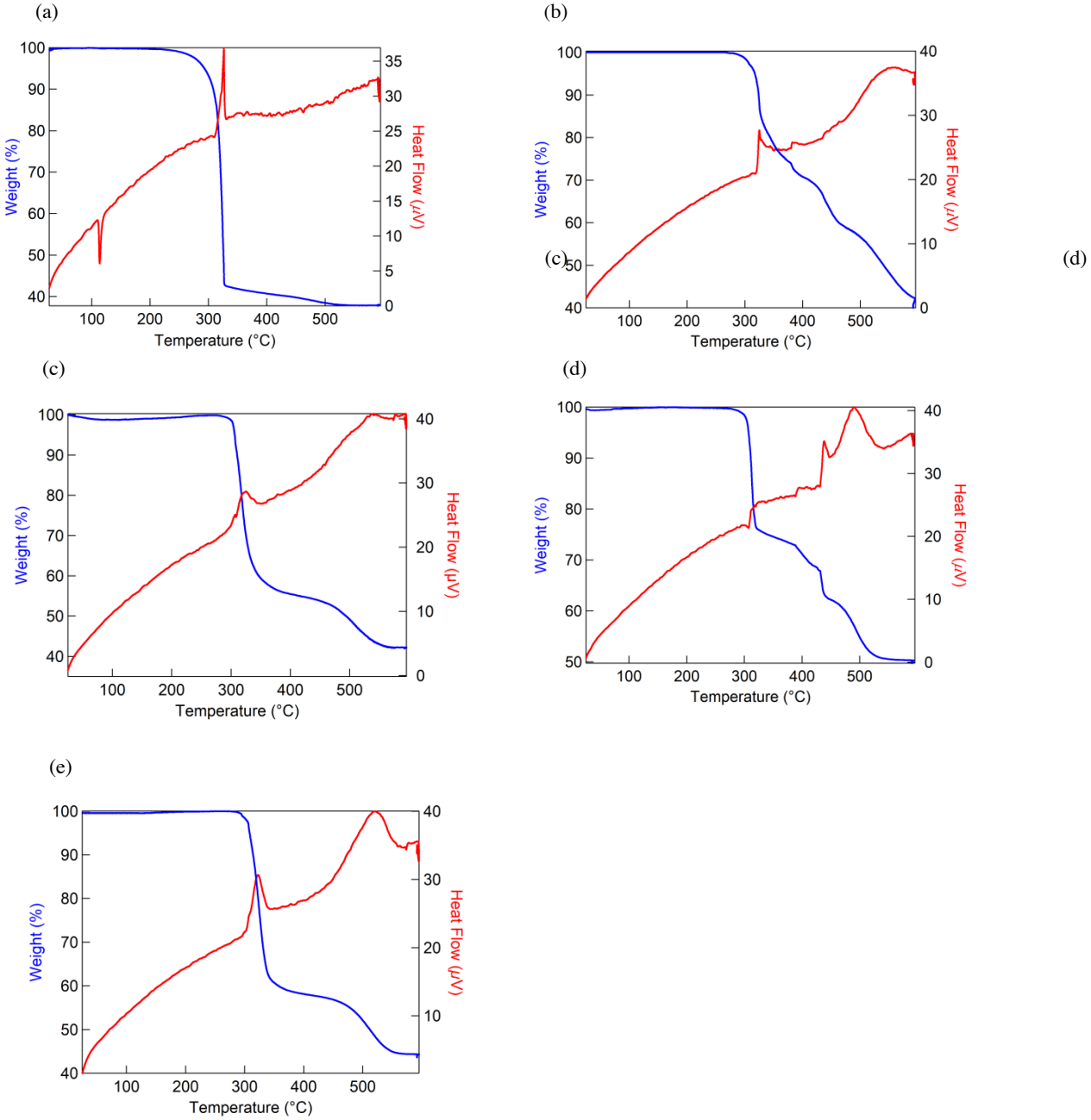


Figure S1. TG/DTA analysis of complexes a) **3**; b) **6a-4**; c) **6a-14**; d) **6b-4**; e) **6b-10** in air (Heating rate, 5.0 °C min^{-1}).

2. DSC analysis

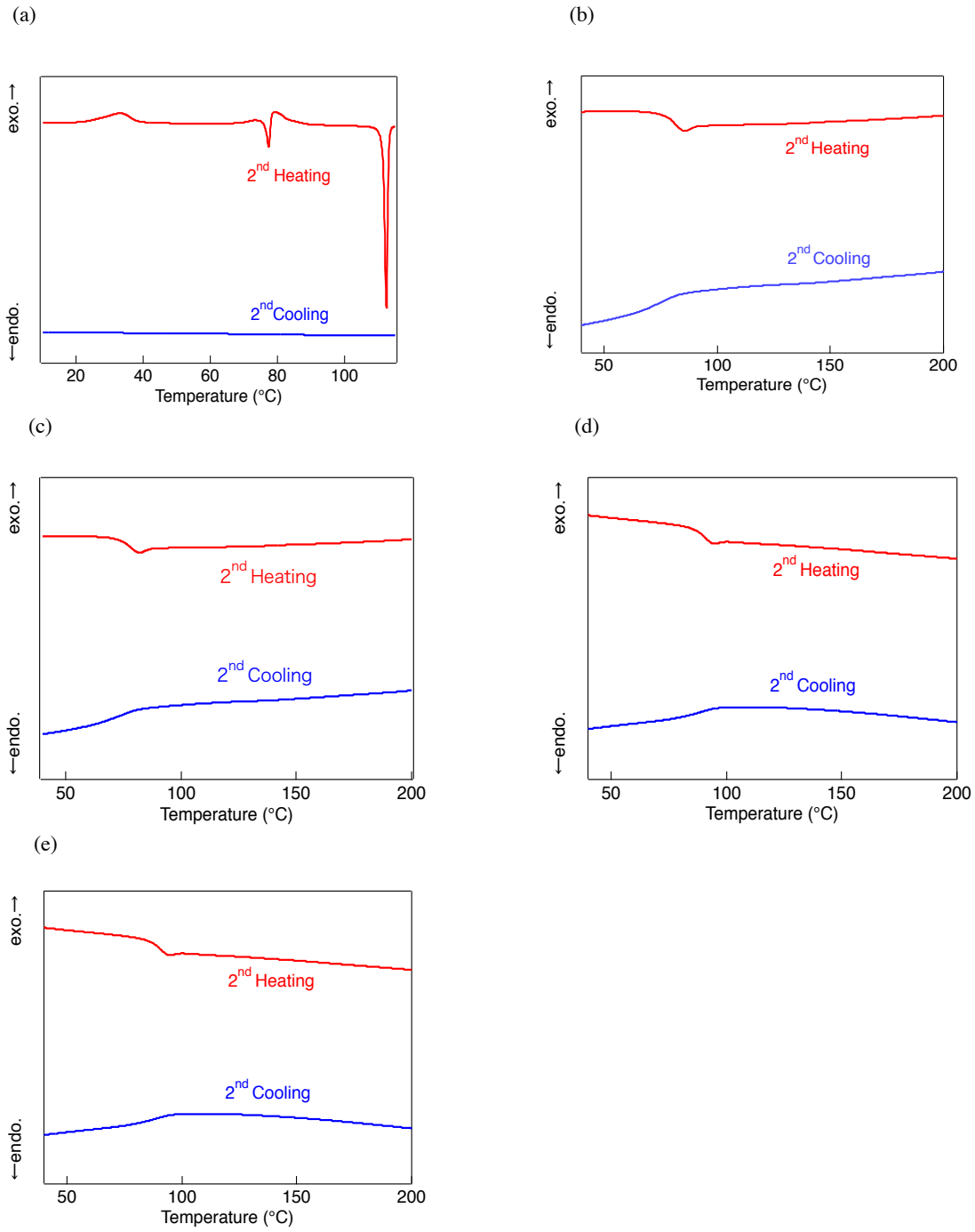


Figure S2. DSC analysis for complexes a) **3**; b) **6a-4**; c) **6a-14**; d) **6b-4**; e) **6b-10** in nitrogen atmosphere (Scan rate, 5.0 °C min^{-1}).

3. ^{1}H NMR studies

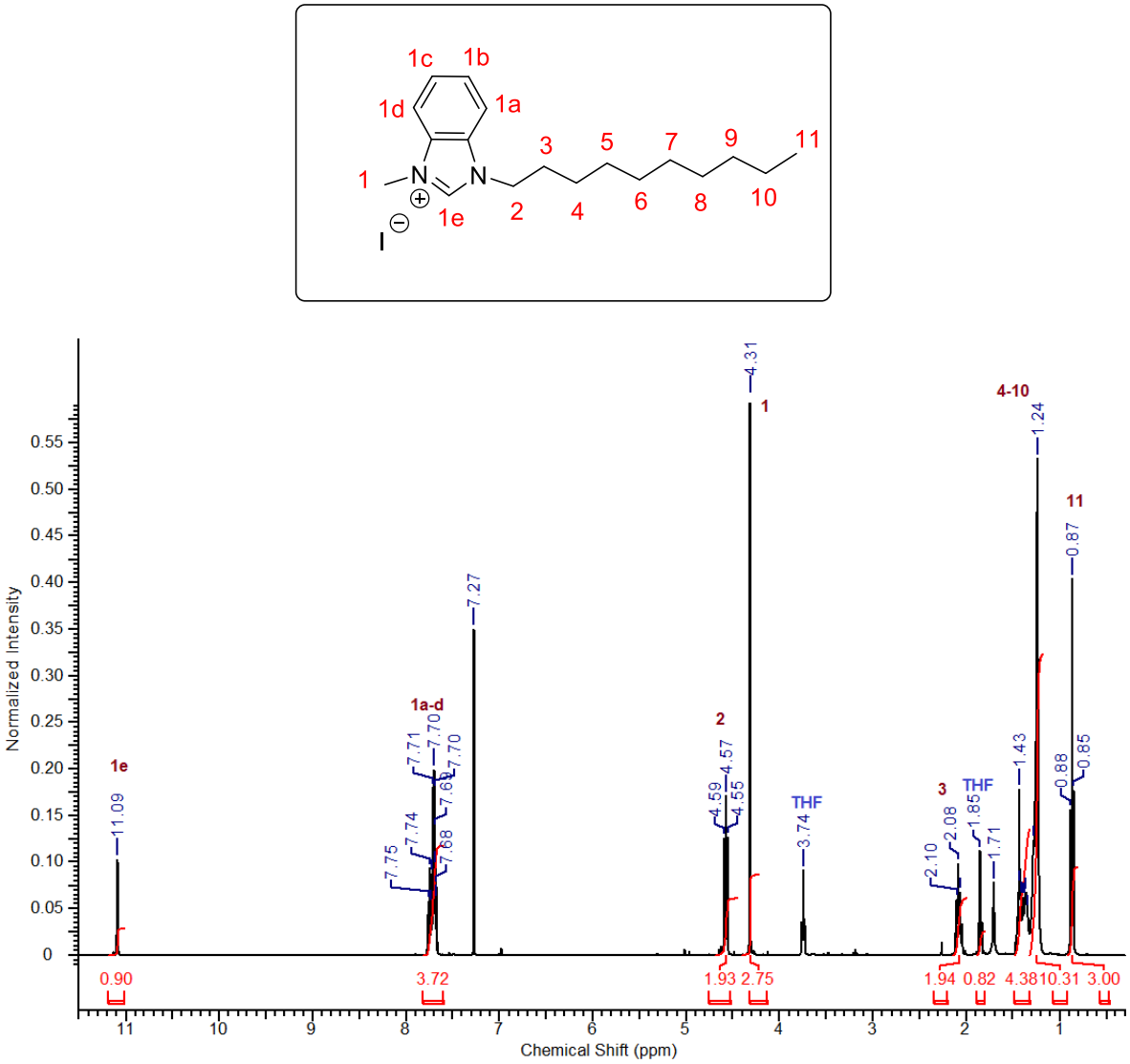


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of salt **2**.

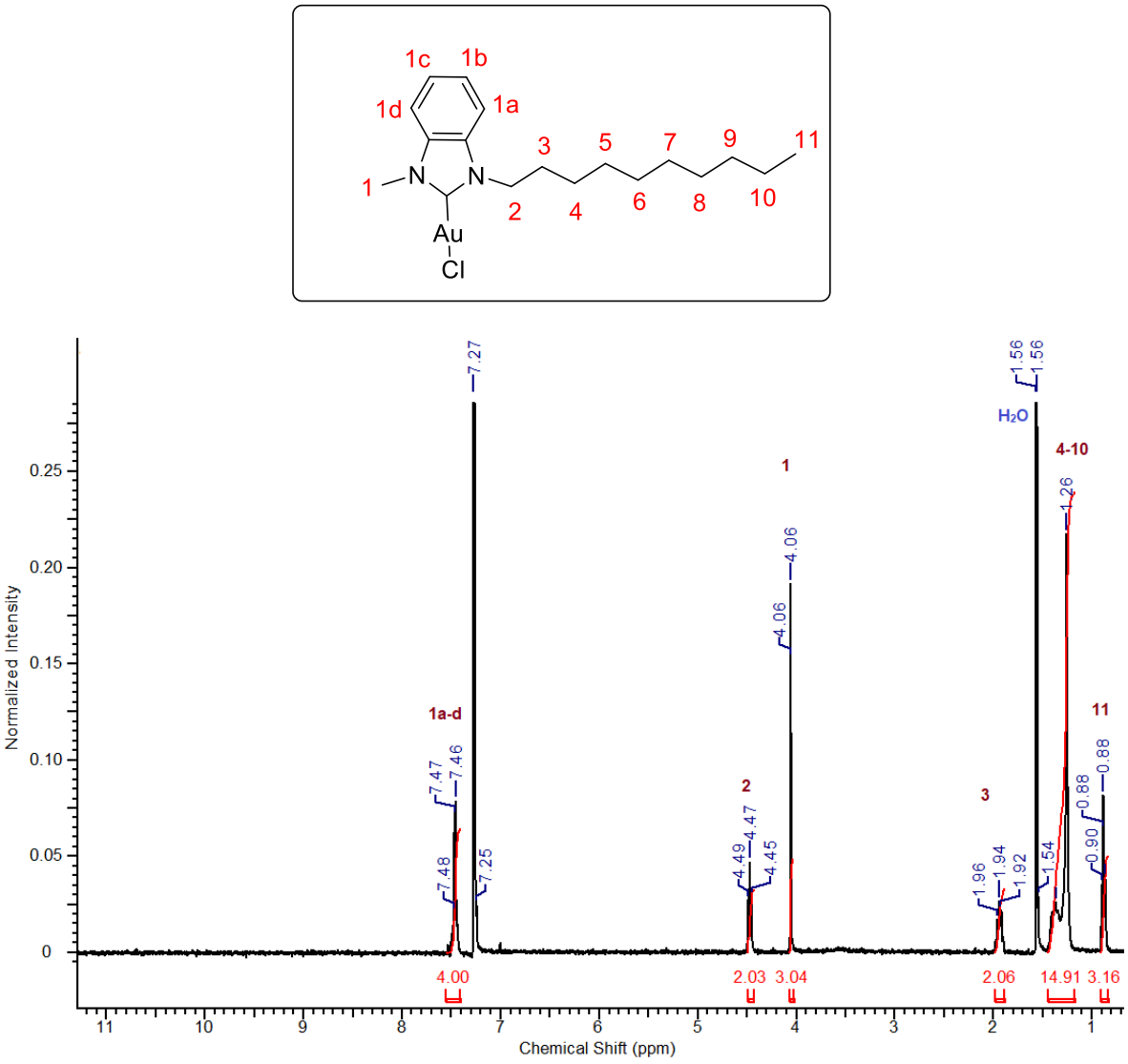


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **3**.

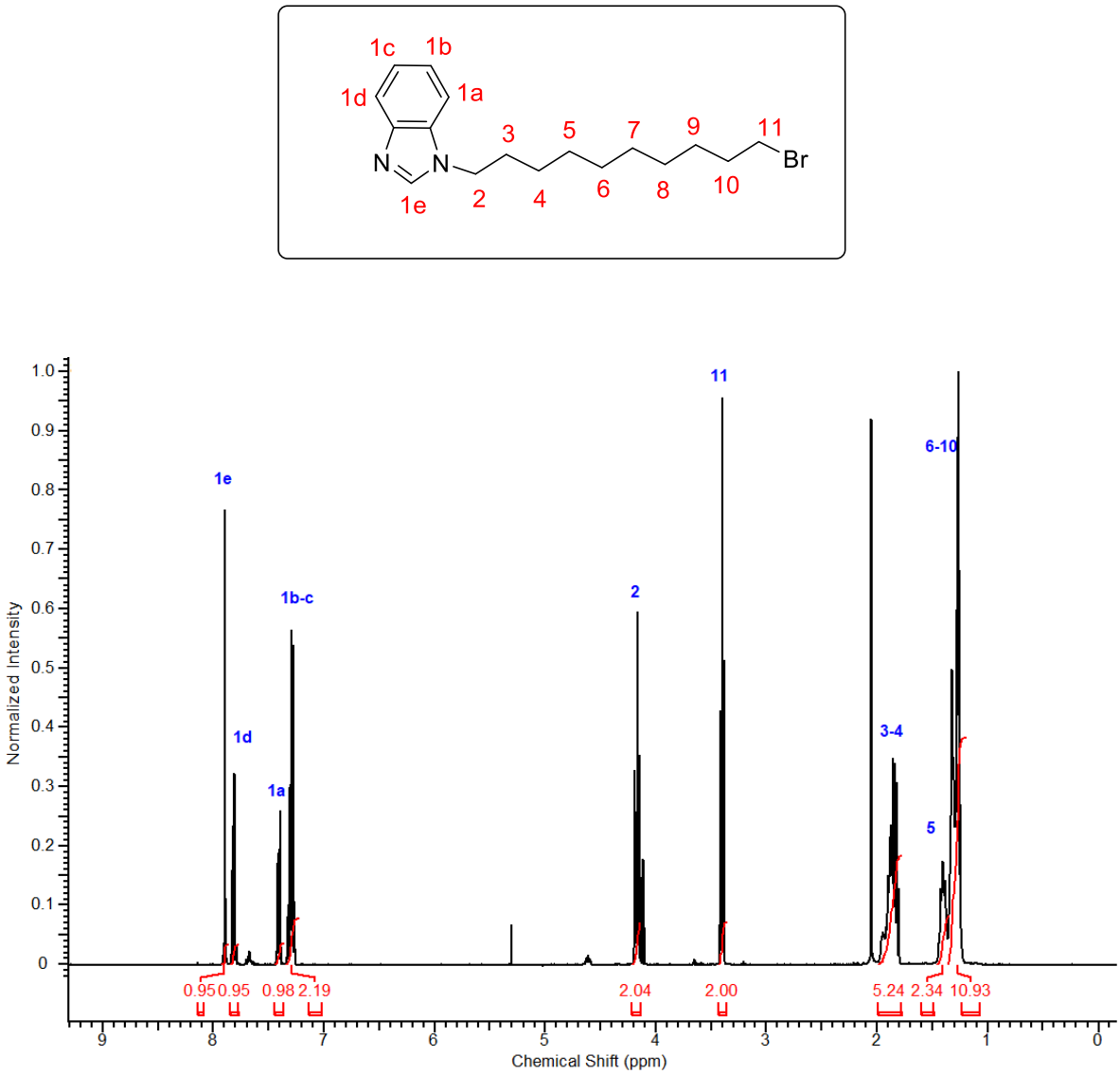


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **4a**.

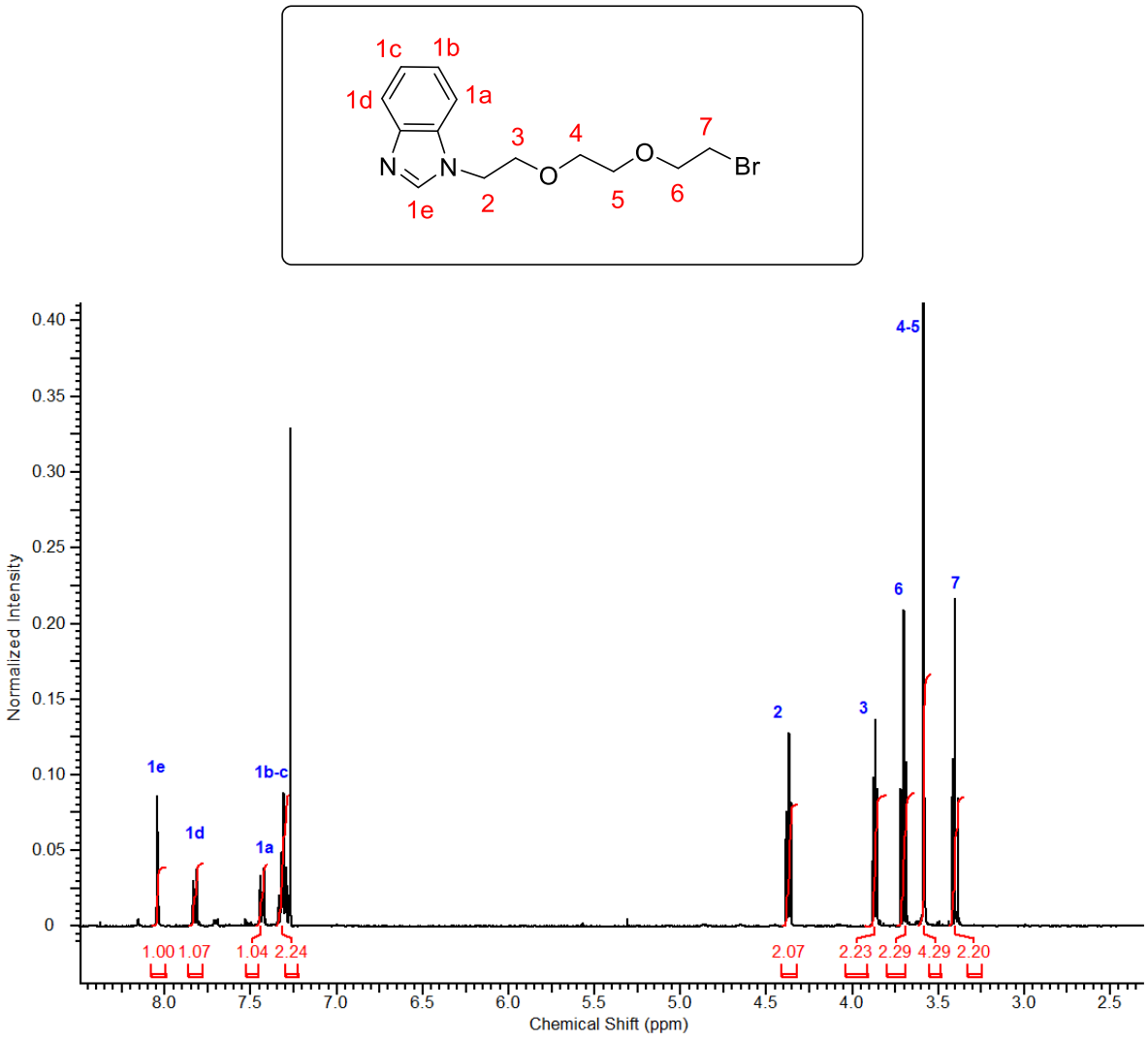
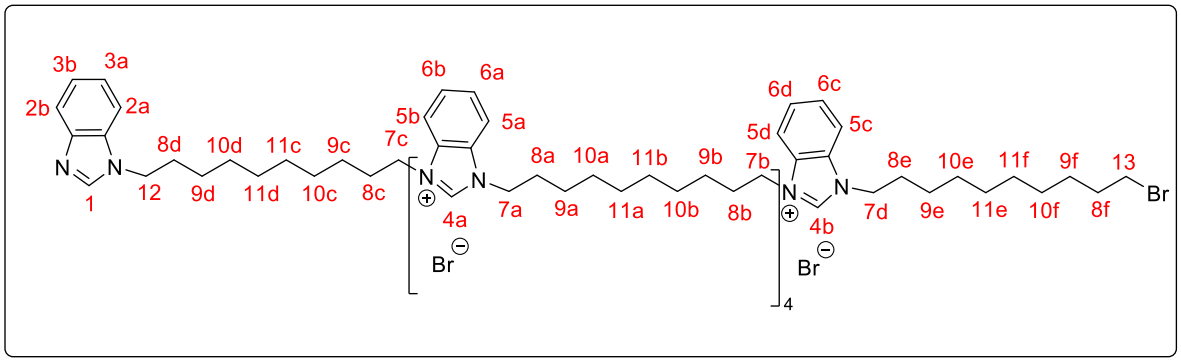


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **4b**.



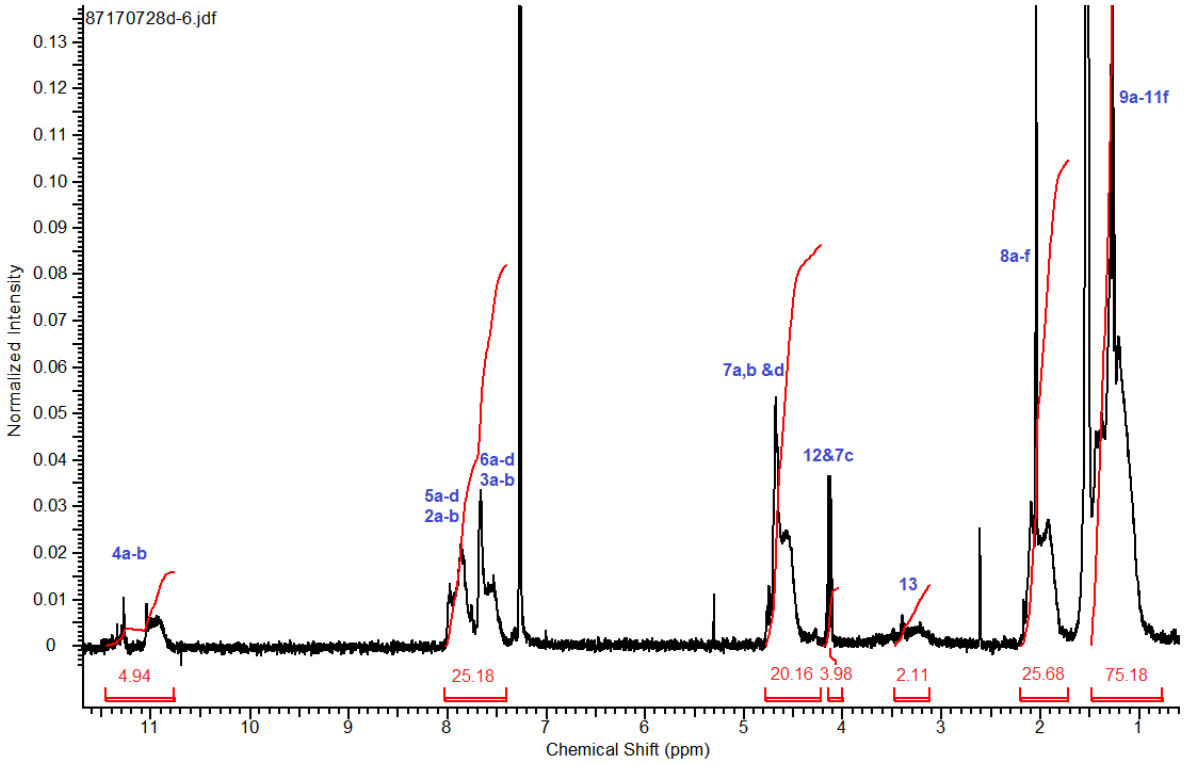


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **5a-4**.

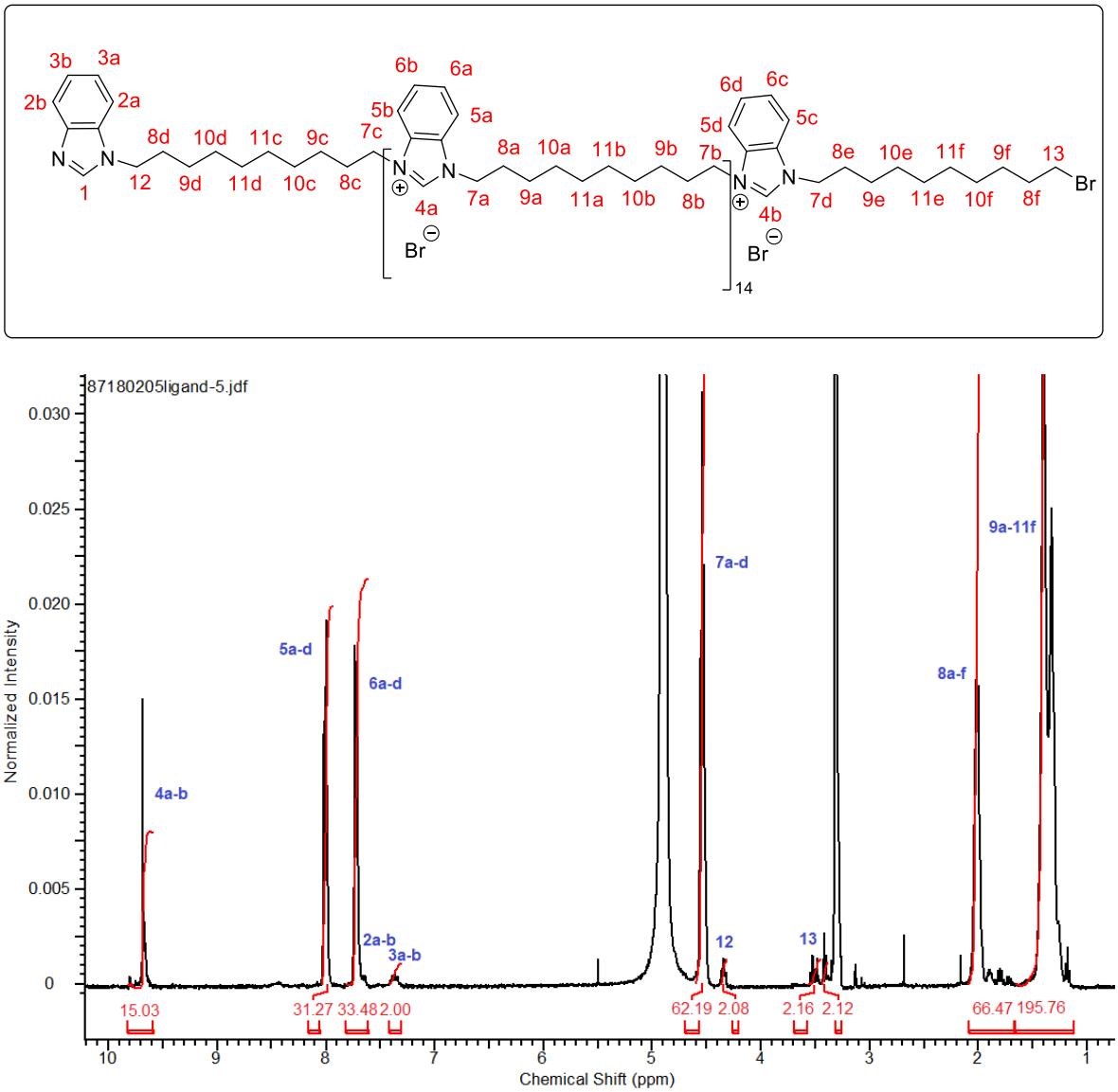
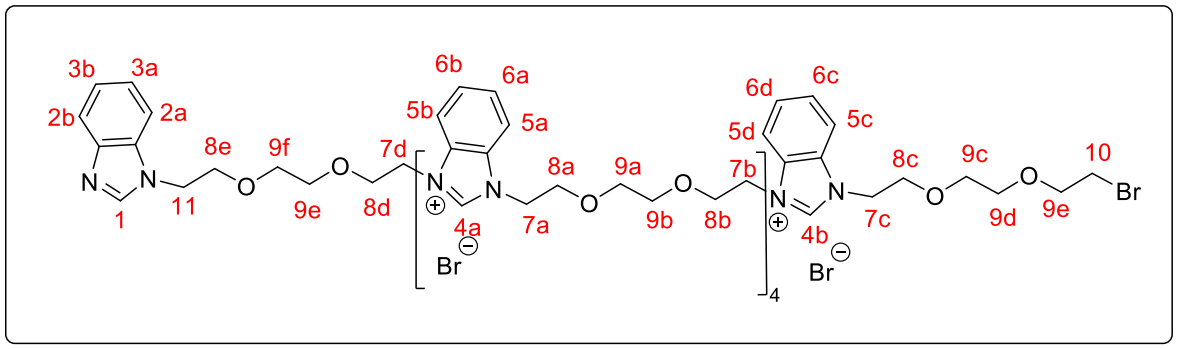


Figure S8. ^{1}H NMR spectrum (400 MHz, Methanol-d_4, rt) of complex **5a-14**.



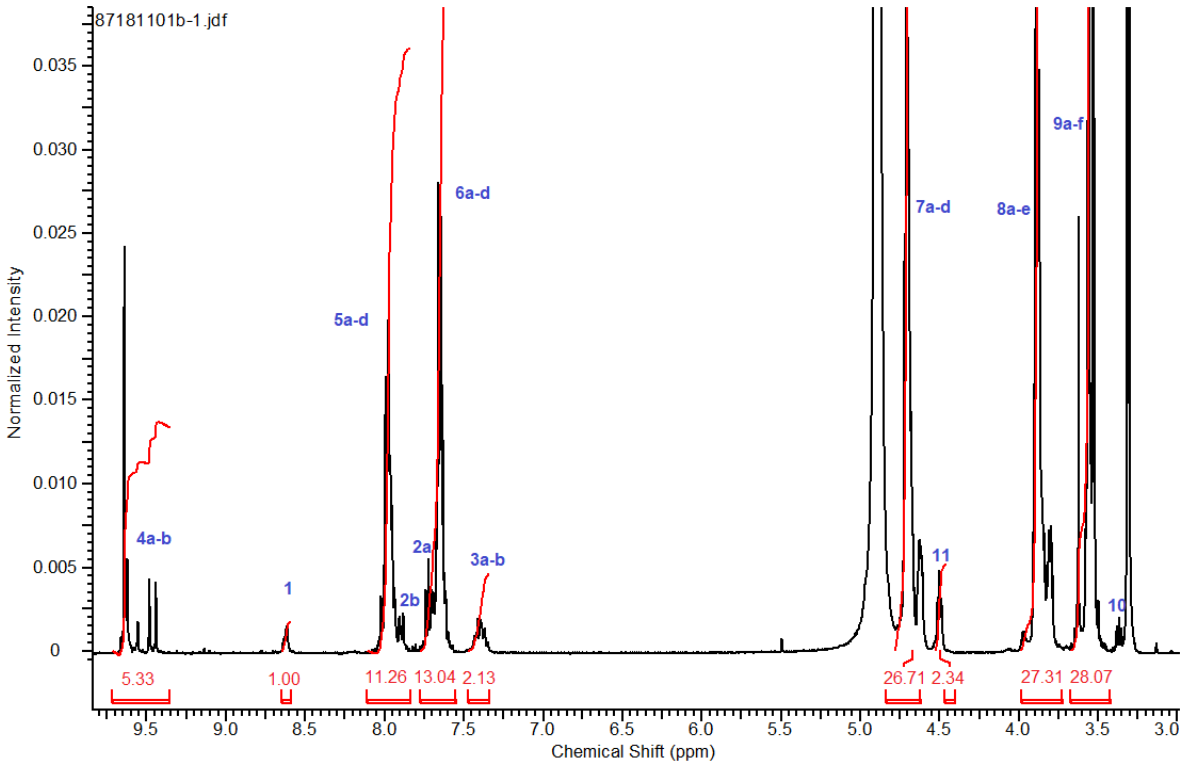
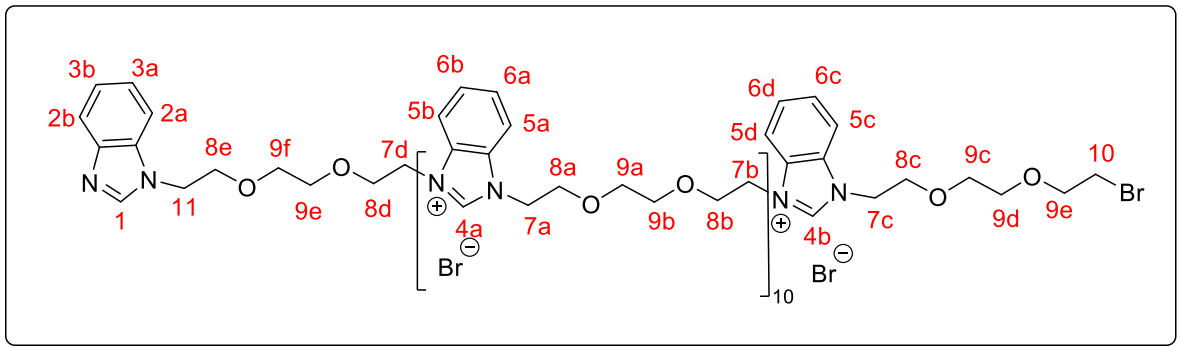


Figure S9. ^{1}H NMR spectrum (400 MHz, Methanol-d_4, rt) of complex **5b-4**.



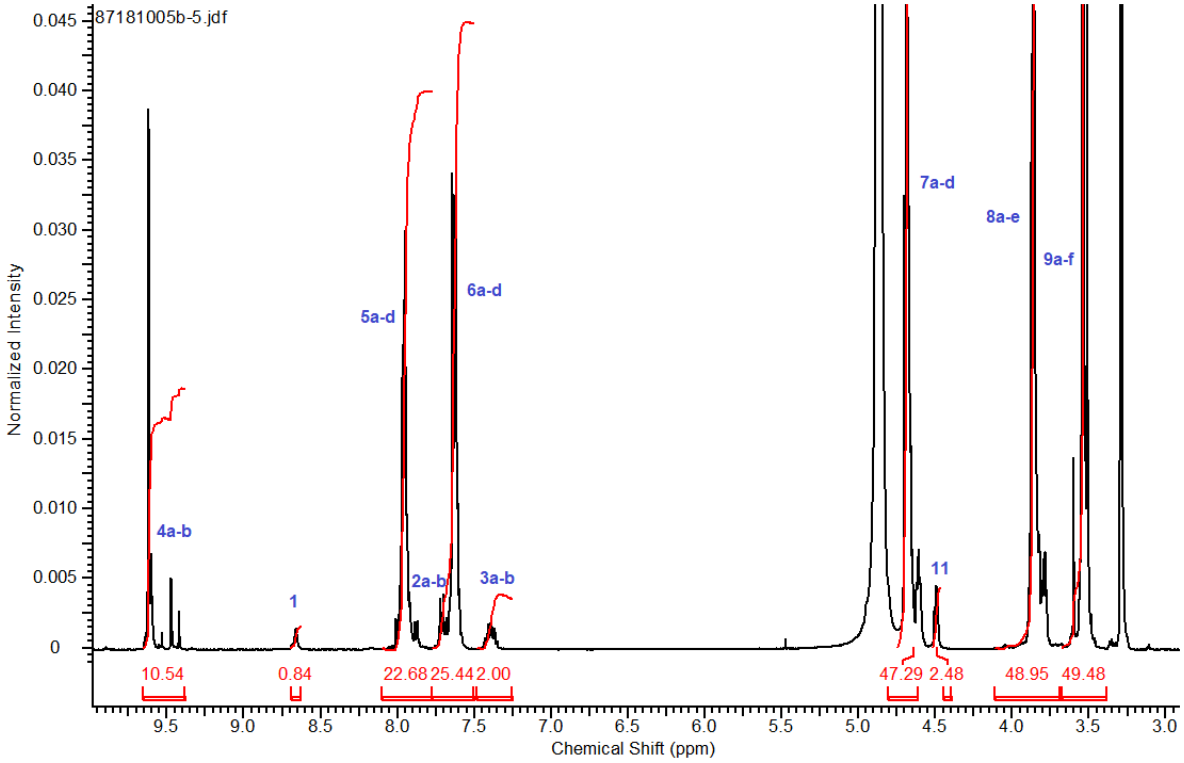


Figure S10. ^{1}H NMR spectrum (400 MHz, Methanol-d_4, rt) of complex **5b-10**.

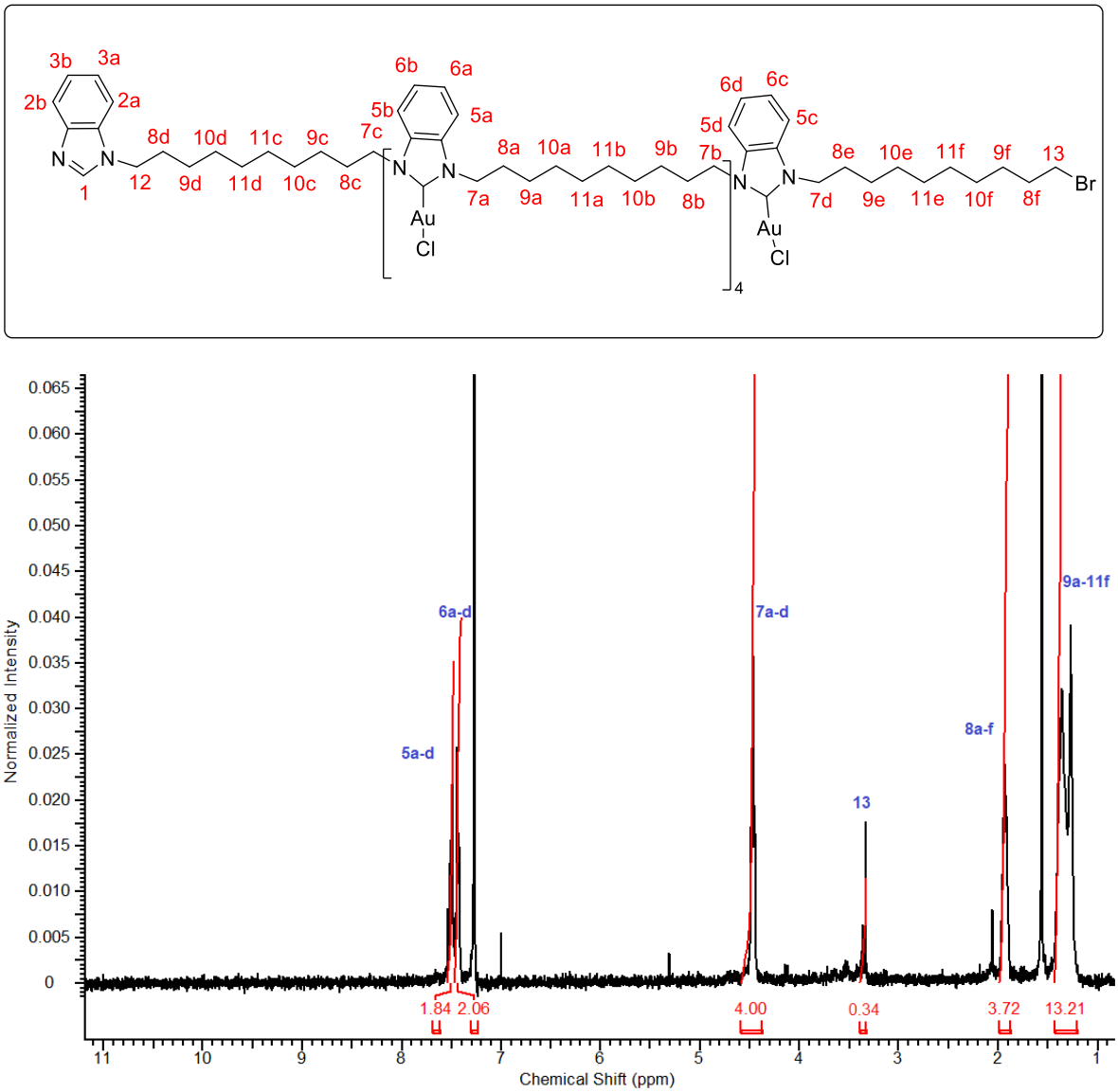


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **6a-4**.

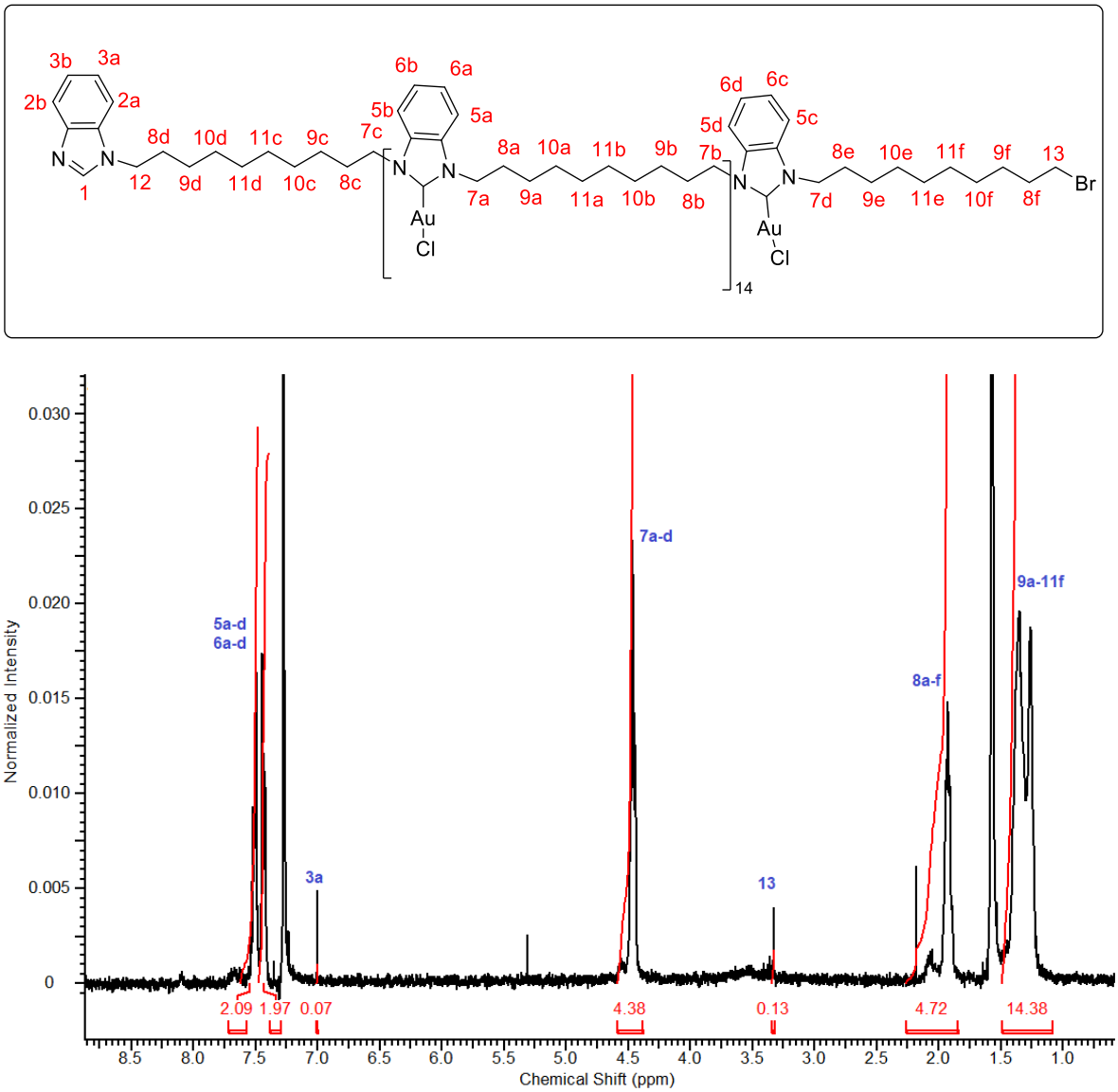


Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **6a-14**.

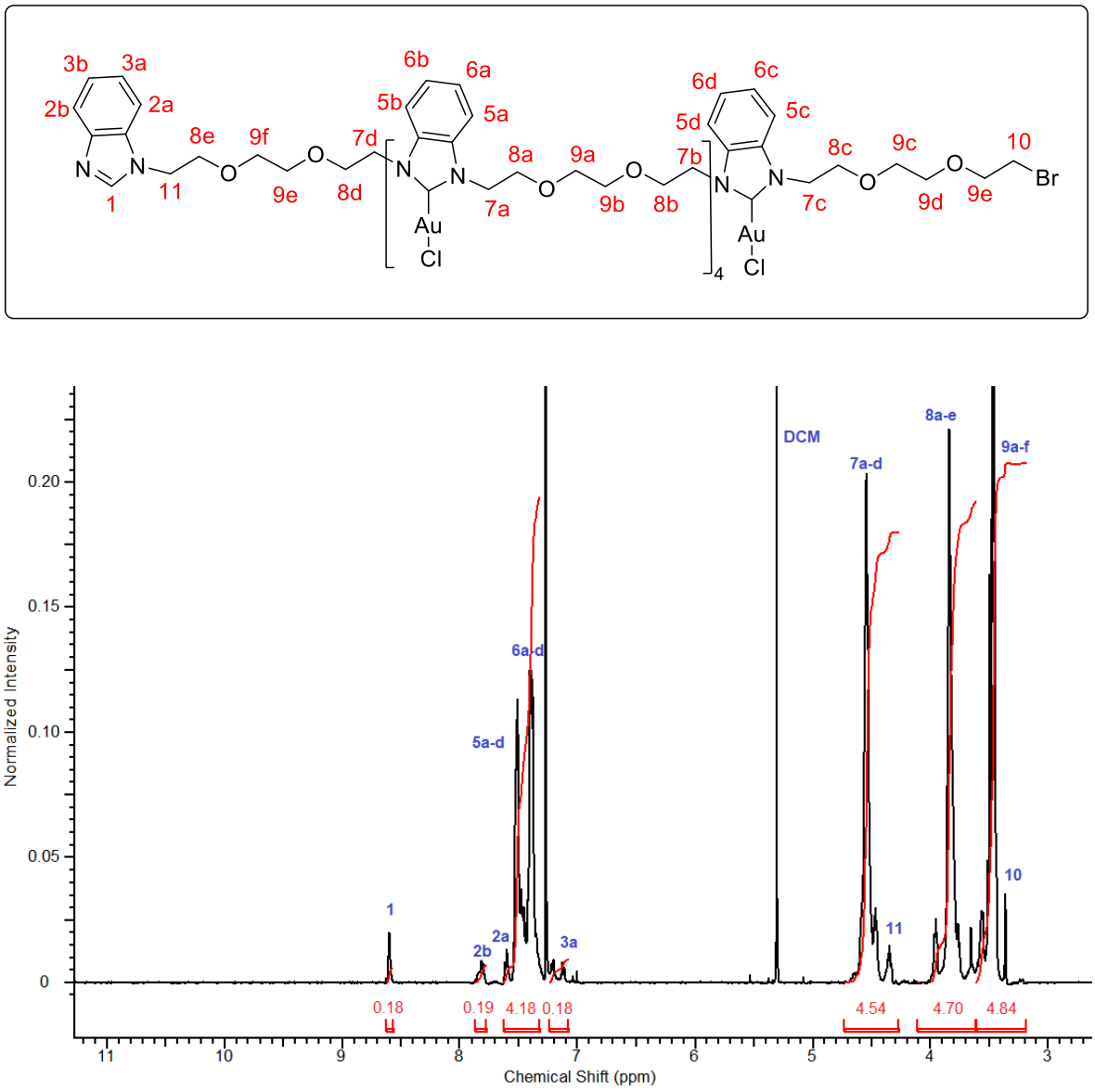


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **6b-4**.

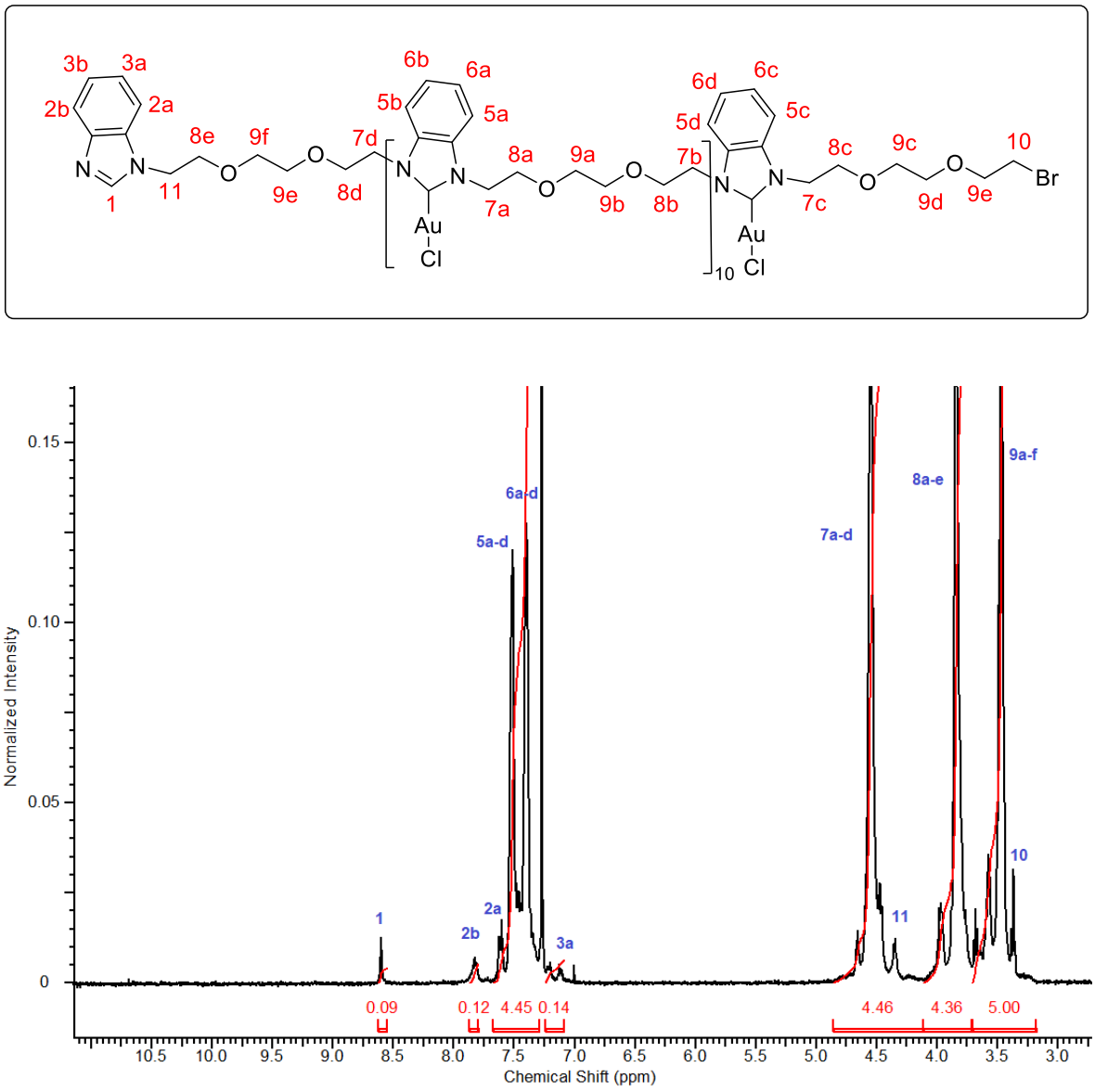


Figure S14: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of complex **6b-10**.

4. Solution state photophysical studies (before and after degassing)

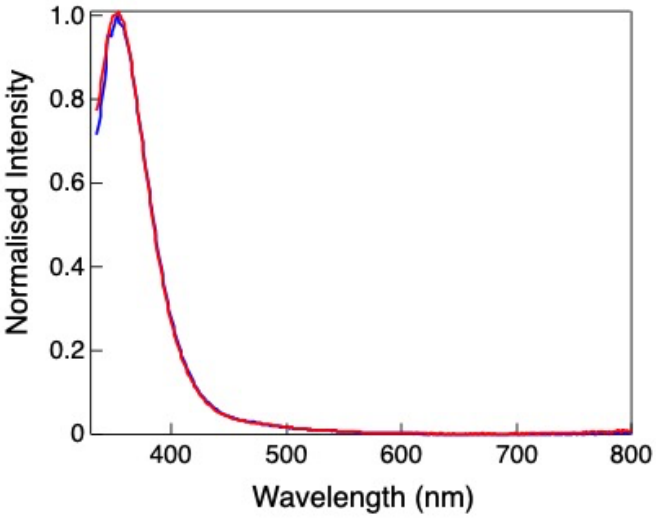


Figure S15. Solution state emission study of complex **3** in CH_2Cl_2 solution (1.7×10^{-6} mol L^{-1}) before and after degassing (red, before degassing; blue, after degassing) at λ_{ex} = 280 nm.

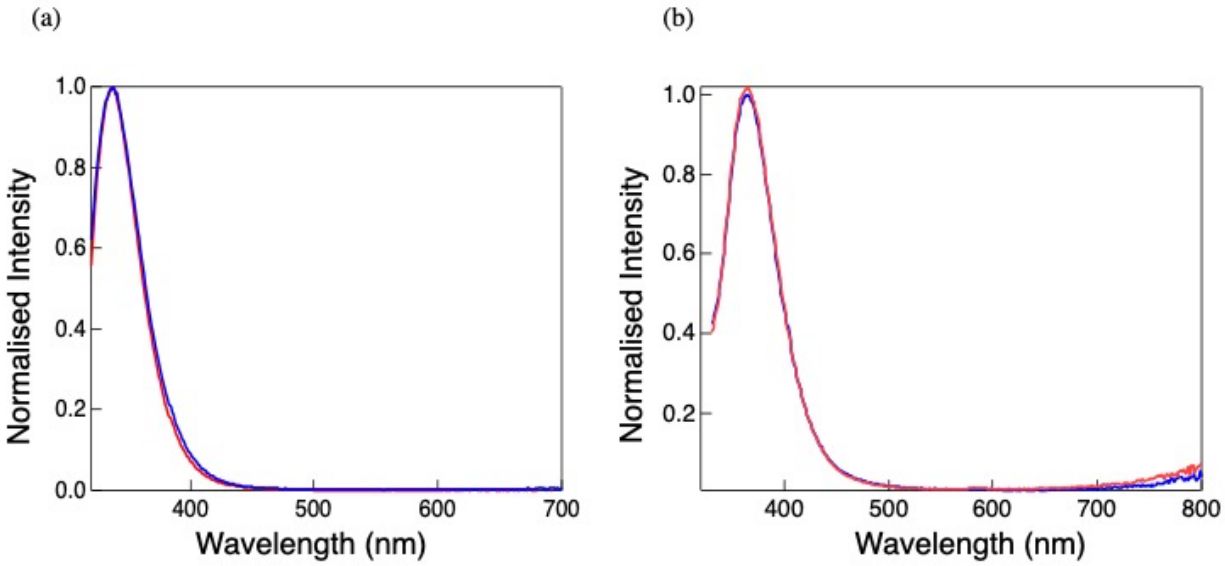


Figure S16. Solution state emission study of complexes in CH_2Cl_2 solution (a) **6a-4** (2.5×10^{-6} mol L^{-1})**,** (b) **6a-14** (6.0×10^{-6} mol L^{-1}) before and after degassing (red, before degassing; blue, after degassing) at λ_{ex} = 280 nm.

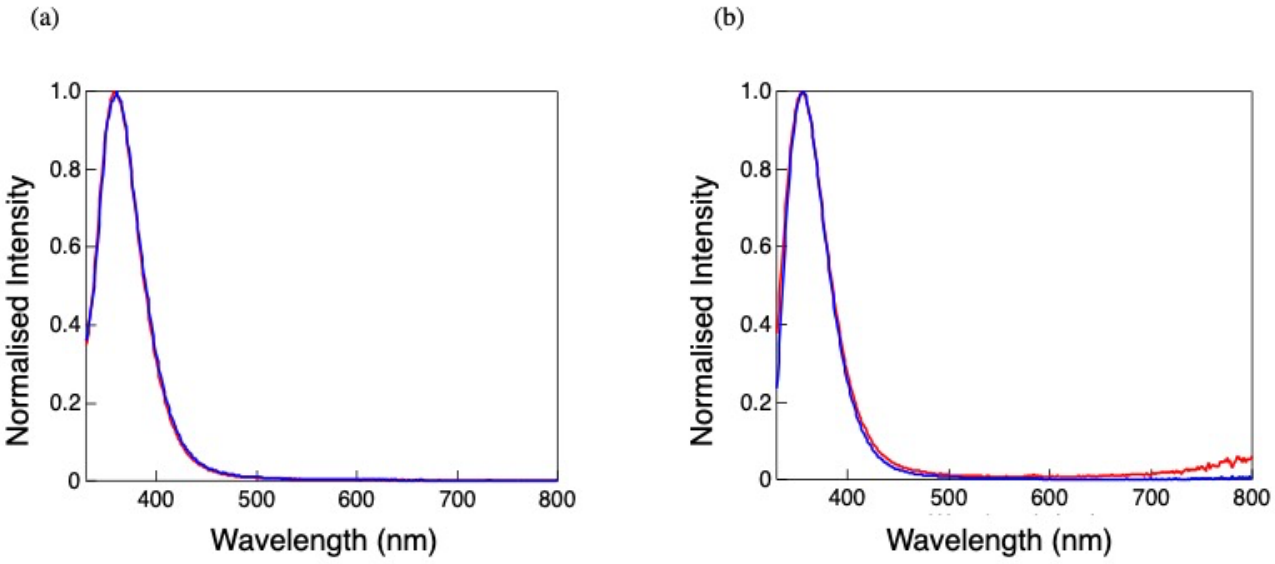
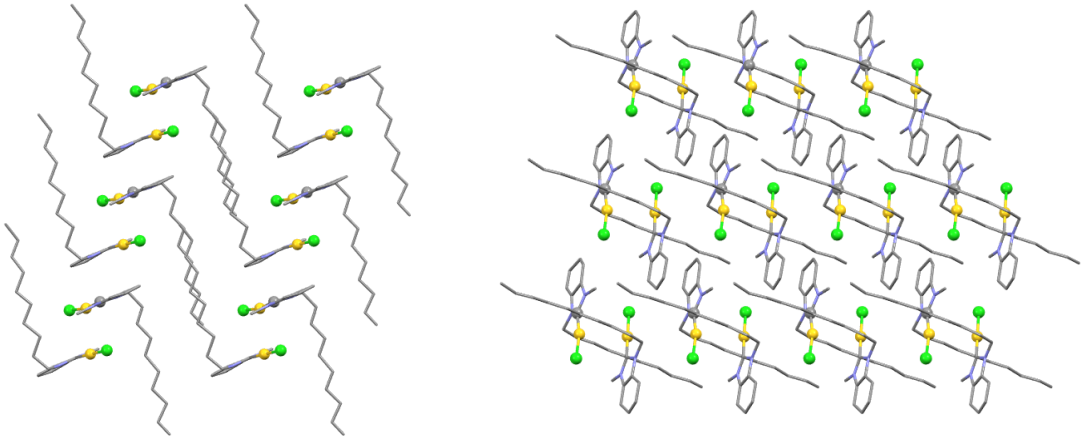


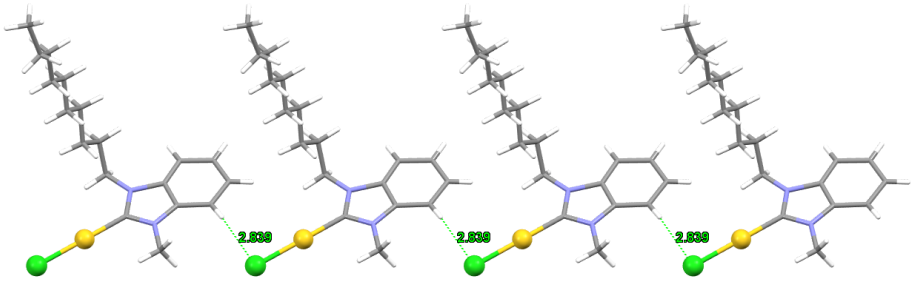
Figure S17. Solution state emission study of complexes in CH_2Cl_2 solution **(a) 6b-4** (4.3×10^{-6} mol L^{-1})**, (b) 6b-10** (8.5×10^{-6} mol L^{-1}) before and after degassing (red, before degassing; blue, after degassing) at λ_{ex} = 280 nm.

5. SCXRD Analysis

(a)



(b)



(c)

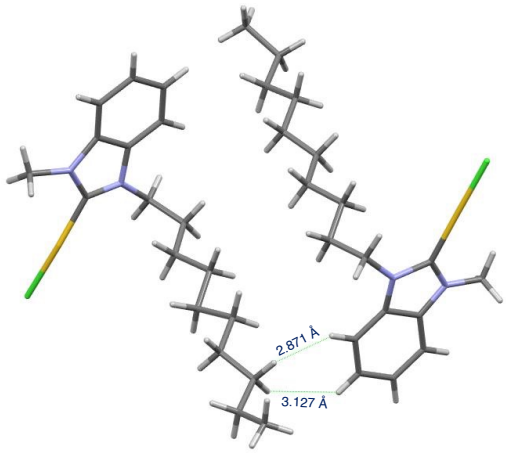


Figure S18. **(a)** Molecular packing of complex **3** with view along b-axis (left) and along c-axis (right); **(b)** Intermolecular interactions of complex **3** showing intermolecular Cl···H interactions; **(c)** Intermolecular H-bonding interactions between *N*-methyl moieties and aromatic benzimidazole ring C–H···C BIM group.

Table S1, Crystal description of complex **3**

Empirical formula	$C_{18}H28AuClN_2$
Formula weight	504.86
Temperature (K)	296
Colour, Habit	Colourless, needle
Crystal size (mm)	0.16 × 0.13 × 0.08
Crystal system	Triclinic
$R[F^2 > 2\sigma(F^2)]$	0.0409
$wR(F^2)$	0.114
Space group	Pī
Z	3
a (Å)	8.7010 (5)
b (Å)	9.2023 (6)
c (Å)	13.0929 (5)
α (degree)	96.876 (5)
β (degree)	105.129 (5)
γ (degree)	100.254 (5)
d (g cm^{-3})	2.565
V (Å^3)	1992.5 (15)

6. Phase transition temperature analysis and POM studies

Table S2. Phase transition temperature for the complexes **3**, **6a-4**, **6a-14**, **6b-4** and **6b-10**.

Complex		Phase Transition Temperature (°C)[a]
3	**Heating**	Iso 36 Cry_1 76 Cry_2 111 Iso
	Cooling	Iso
6a-4	**Heating**	Glass 76 Gum
	Cooling	Glass 71 Gum
6a-14	**Heating**	Glass 77 Gum
	Cooling	Glass 78 Gum
6b-4	**Heating**	Glass 89 Gum
	Cooling	Glass 89 Gum
6b-10	**Heating**	Glass 89 Gum
	Cooling	Glass 89 Gum

Abbreviations: Cry: Crystalline; Iso: Isotropic; Glass: Glass state; Gum: Rubber state.
[a]The thermodynamic parameters were determined using differential scanning calorimetry (DSC) (X-DSC7000, SII) at heating and cooling rates of 5.0 °C min^{-1} for complexes **3**, **6a-4**, **6a-14**, **6b-4** and **6b-10**.

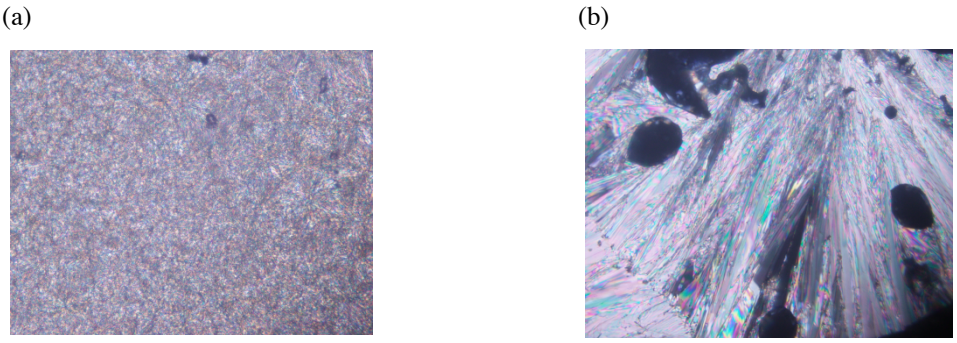


Figure S19. Polarising optical micrographs of complex **3** under crossed polarisers: (**a**) **3** at 45 ℃ in the 2nd heating process (Cry1 phase); (**b**) **3** at 85 ℃ in the 2nd heating process (Cry2 phase). Polarised optical microscopy was carried out using an Olympus BX51 microscope equipped with a temperature-controlled stage (Instec HCS302 microscope hot and cold stage mK1000 temperature controller).

7. Solution state photophysical studies of polymeric complexes

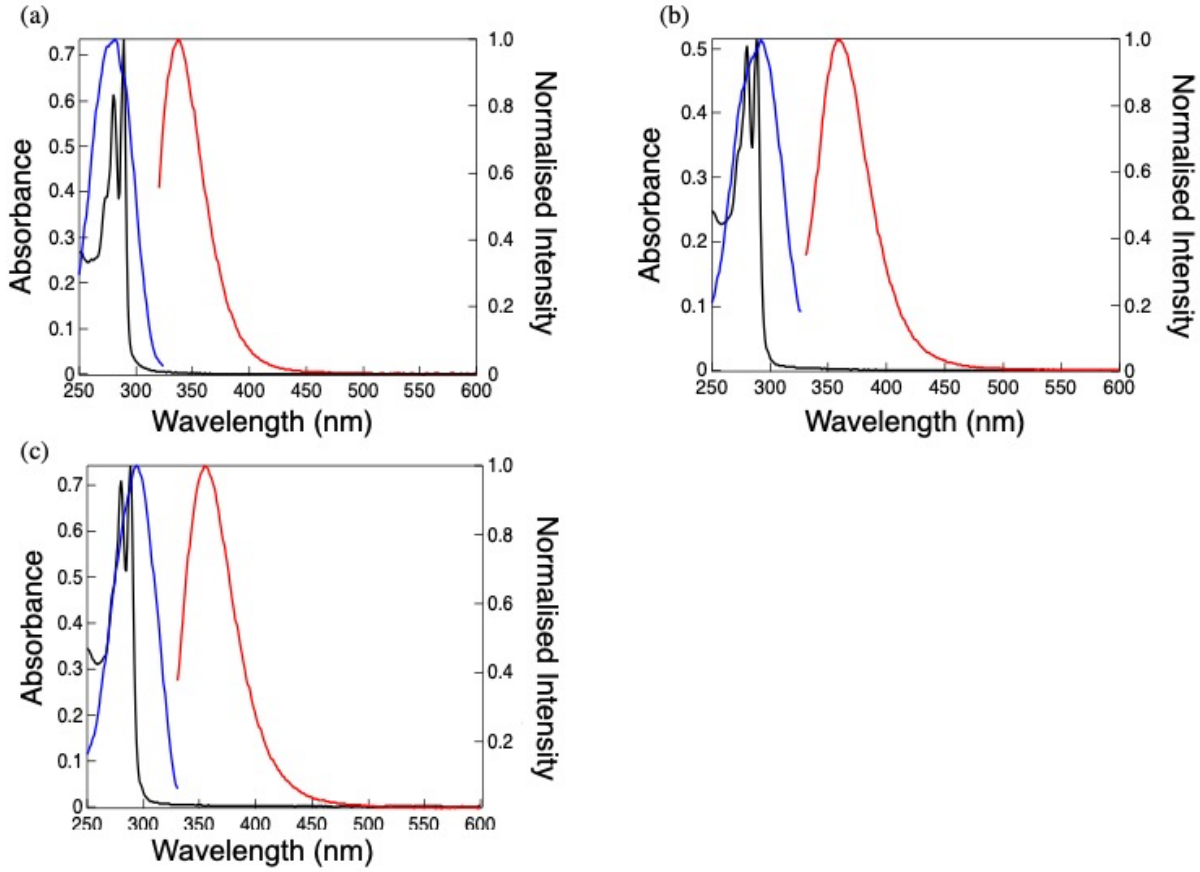


Figure S20. Photophysical properties of complexes in dilute CH_2Cl_2 solution (a) **6a-14** (abs = 6.0×10^{-5} mol L^{-1}, emission = 6.0×10^{-6} mol L^{-1}); (b) **6b-4** (abs = 4.3×10^{-5} mol L^{-1}, emission = 4.3×10^{-6} mol L^{-1}); (c) **6b-10** (abs = 8.5×10^{-5} mol L^{-1}, emission = 8.5×10^{-6} mol L^{-1}). Black, absorption spectra; blue, excitation spectra; red, emission spectra.

8. Structure of complex $Me_2BIAu(I)Cl$

(a) (b)

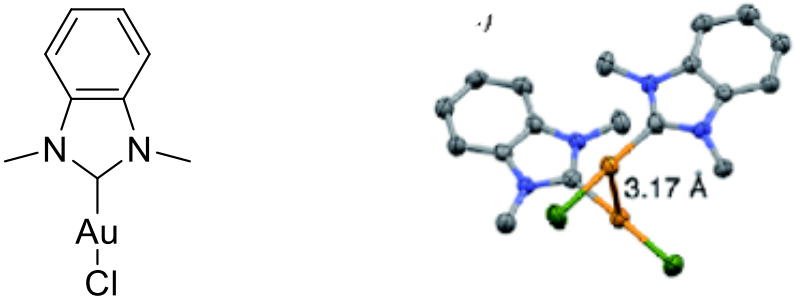


Figure S21. (**a**) Molecular structure of complex **$Me_2BIAu(I)Cl$**. (**b**) Crystal structure of complex **$Me_2BIAu(I)Cl$**.[1]

9. Lifetime decay curves

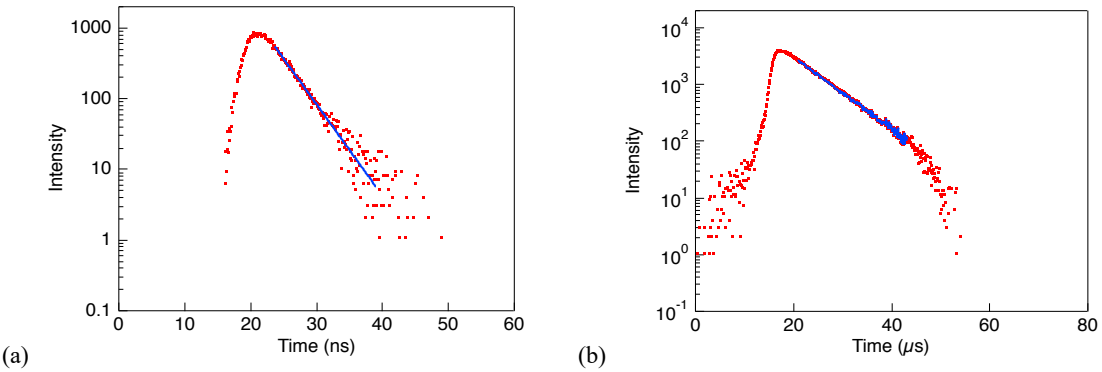


Figure S22. Decay profiles (red) and fitting curves (blue) of complex **3** in solid. Measurement wavelength: (a) 380-500 nm, (b) 500-800 nm.

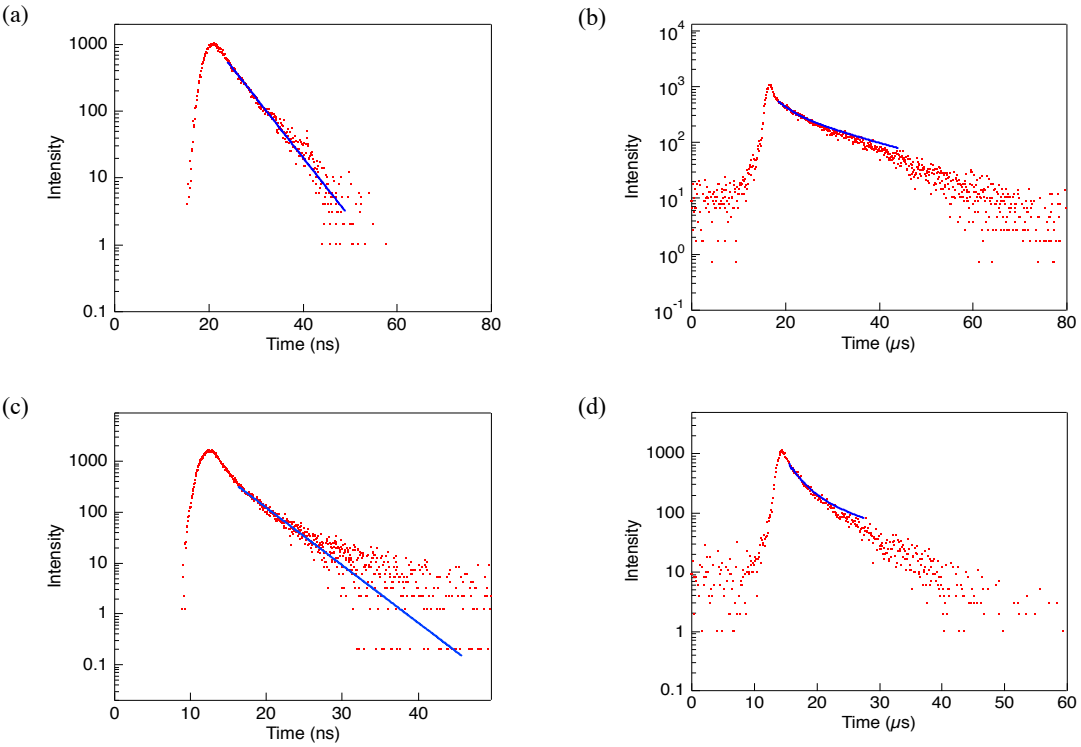


Figure S23: Decay profiles (red) and fitting curves (blue) of complexes in solid: (a, b) **6a-4**, (c, d) **6a-14**. Measurement wavelength: (a) 380-560 nm, (b) 560-800 nm, (c) 400-500 nm, (d) 600-800 nm.

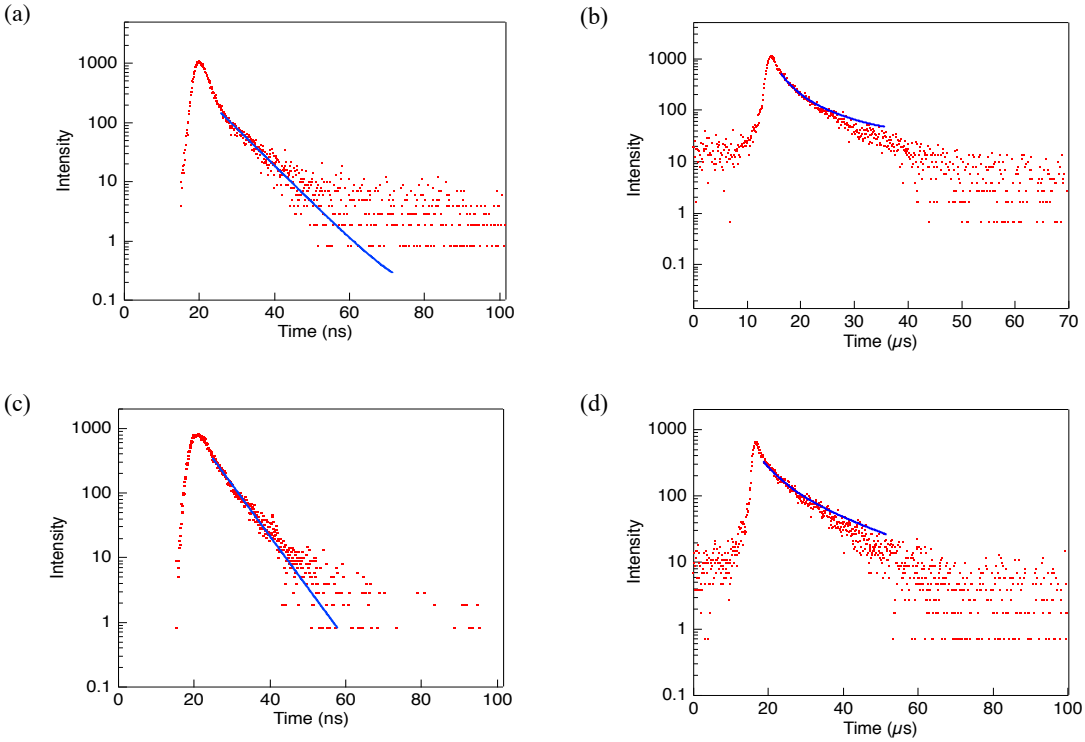


Figure S24. Decay profiles (red) and fitting curves (blue) of complexes in solid: (a, b) **6b-4**, (c, d) **6b-14**. Measurement wavelength: (a) 400-500 nm, (b) 600-800 nm, (c) 400-500 nm, (d) 600-800 nm.

10. PXRD Analysis

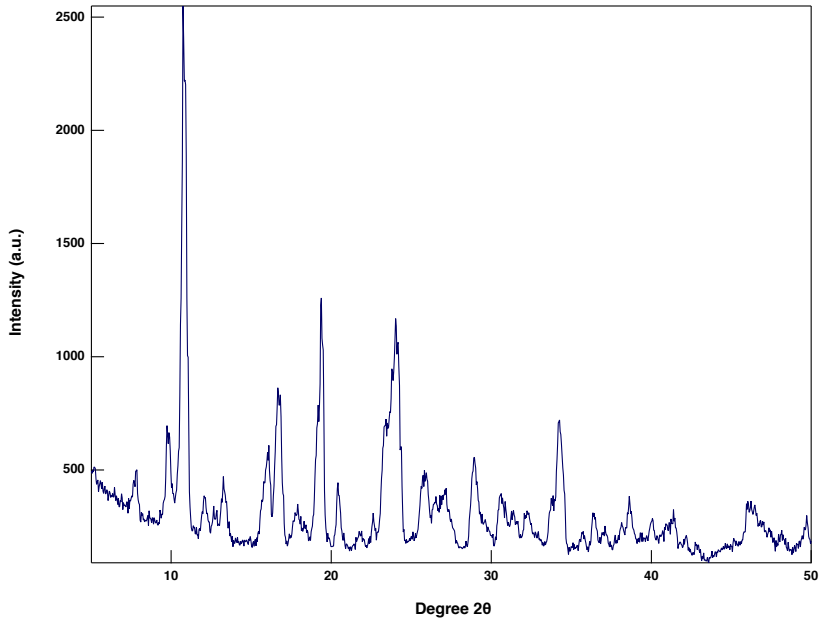


Figure S25. PXRD analysis of complex **3** at rt.

11. CIE Plot

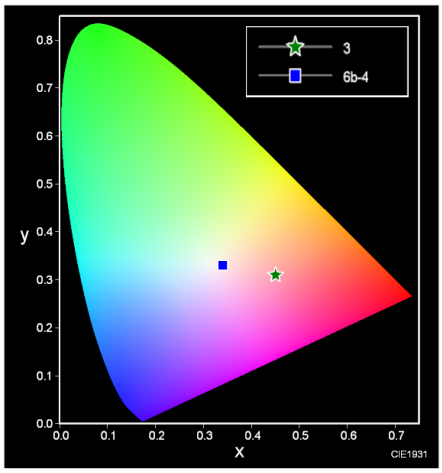


Figure S26. CIE plot of complex **3** with CIE coordinates of (x, y) = (0.45,0.31) and **6b-4** with (0.34,0.33) in solid state.

12. References

1. A. Sathyanarayana, S.-Y. Nakamura, K. Hisano, O. Tsutsumi, K. Srinivas and G. Prabusankar, *Sci*. *China Chem*., 2018, **61**, 957