Supporting Information

Aluminium(III) Porphyrin Based Axial-Bonding Type Dyads Containing Thiaporphyrins and Expanded Thiaporphyrins as Axial Ligands

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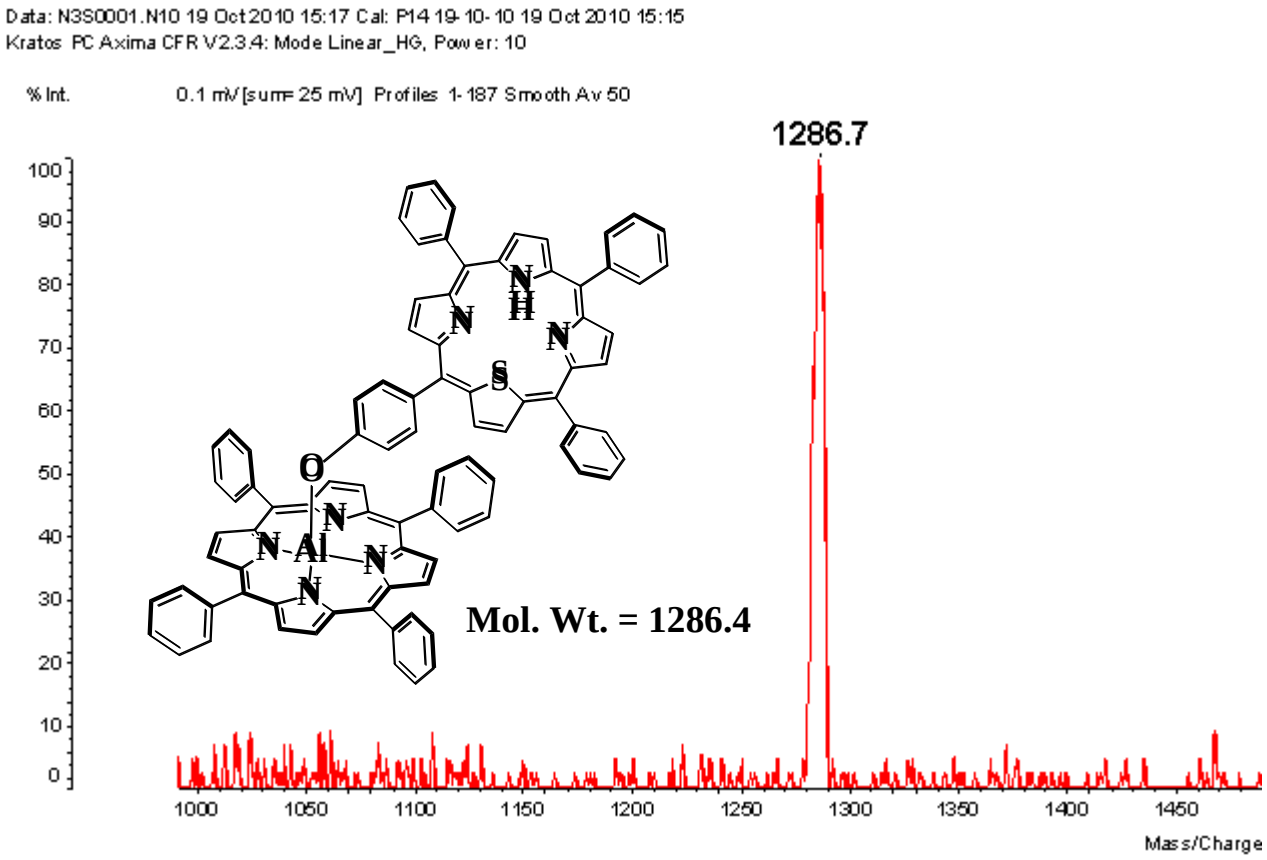


Figure S1. MALDI –TOF mass spectrum of dyad **1**.

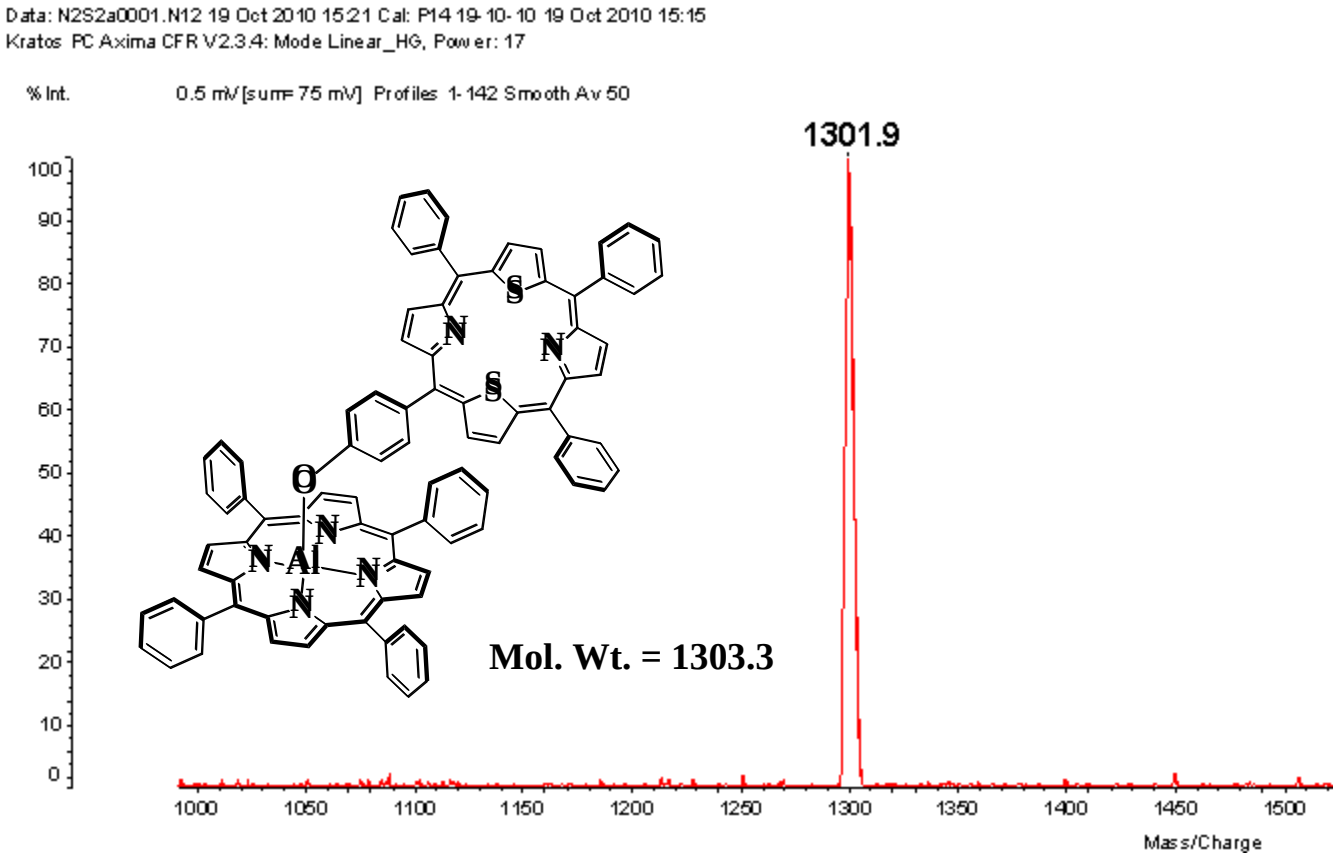


Figure S2. MALDI –TOF mass spectrum of dyad **2**.

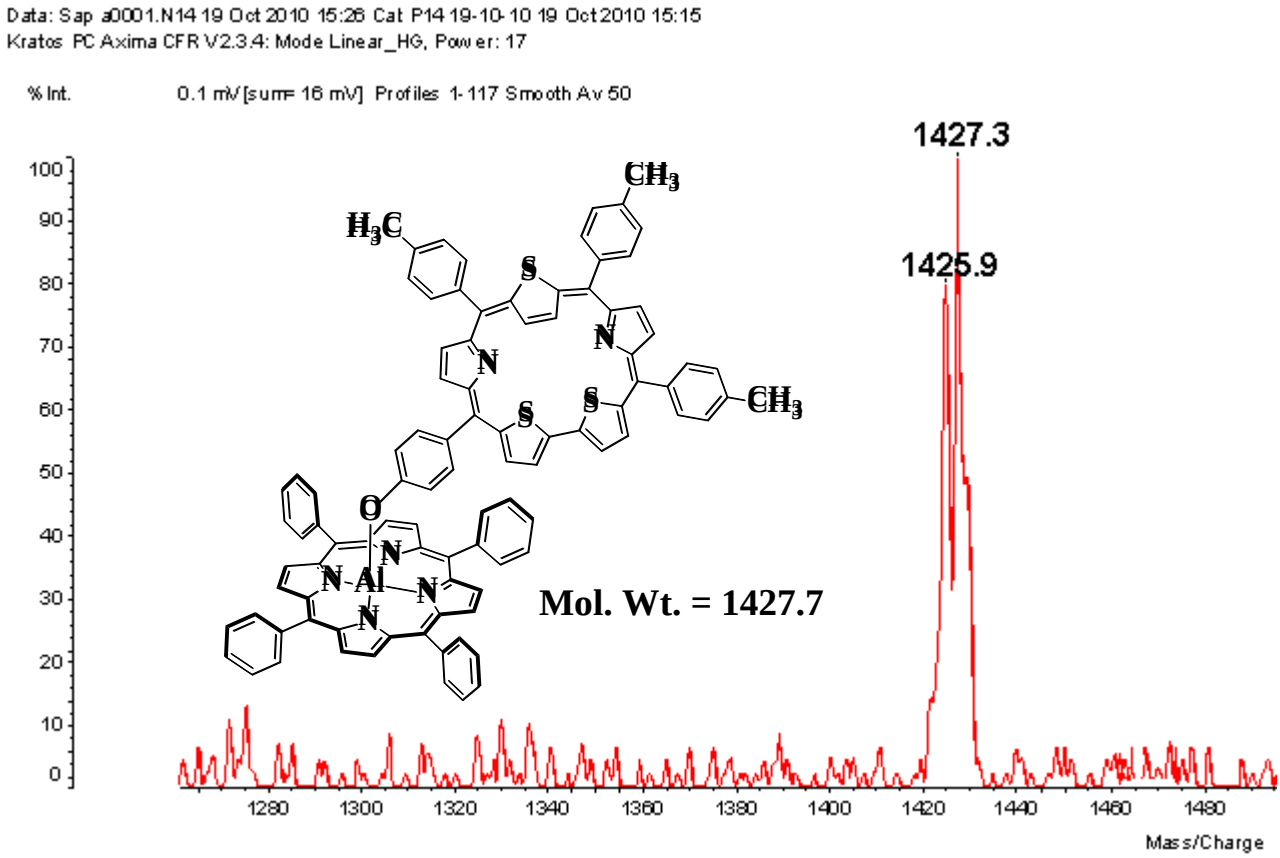


Figure S3. MALDI –TOF mass spectrum of dyad **3**.

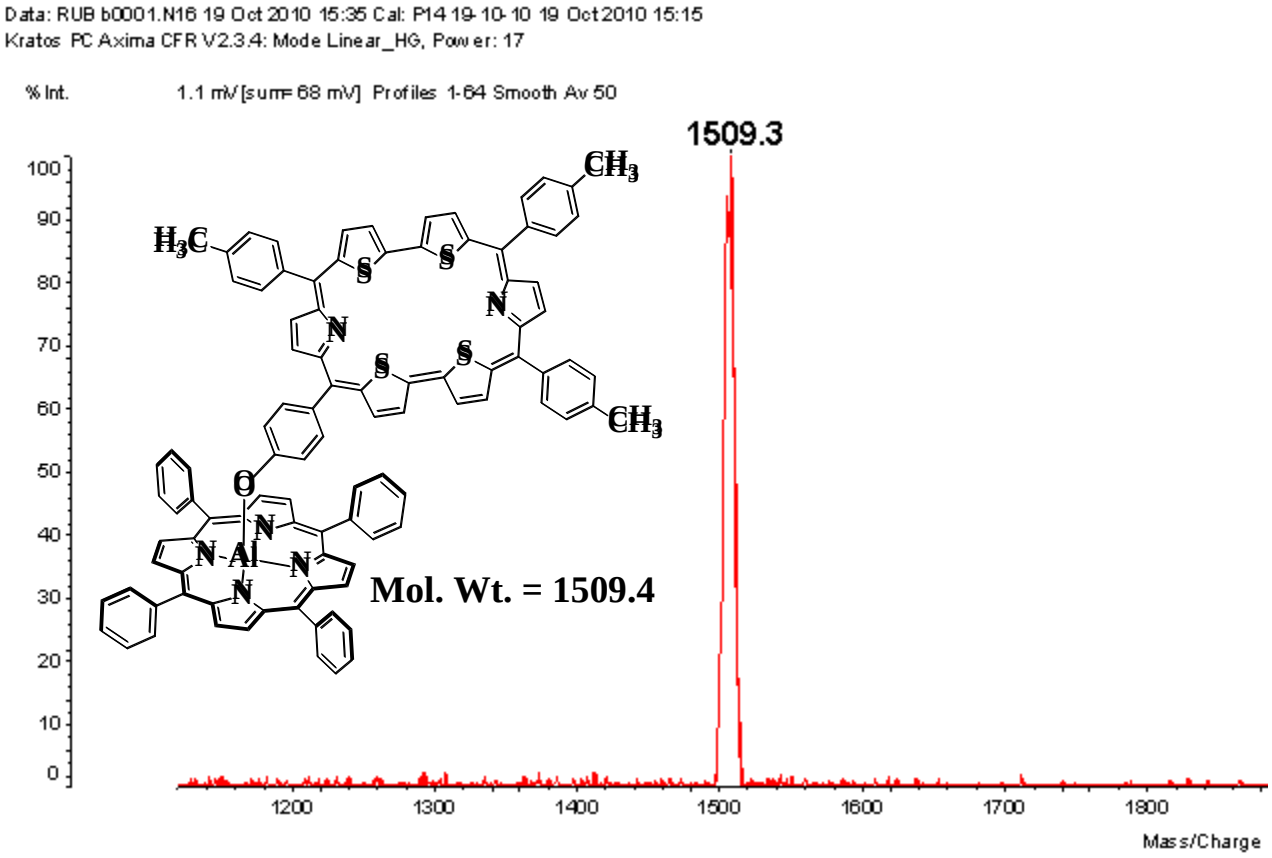


Figure S4. MALDI –TOF mass spectrum of dyad **4**.

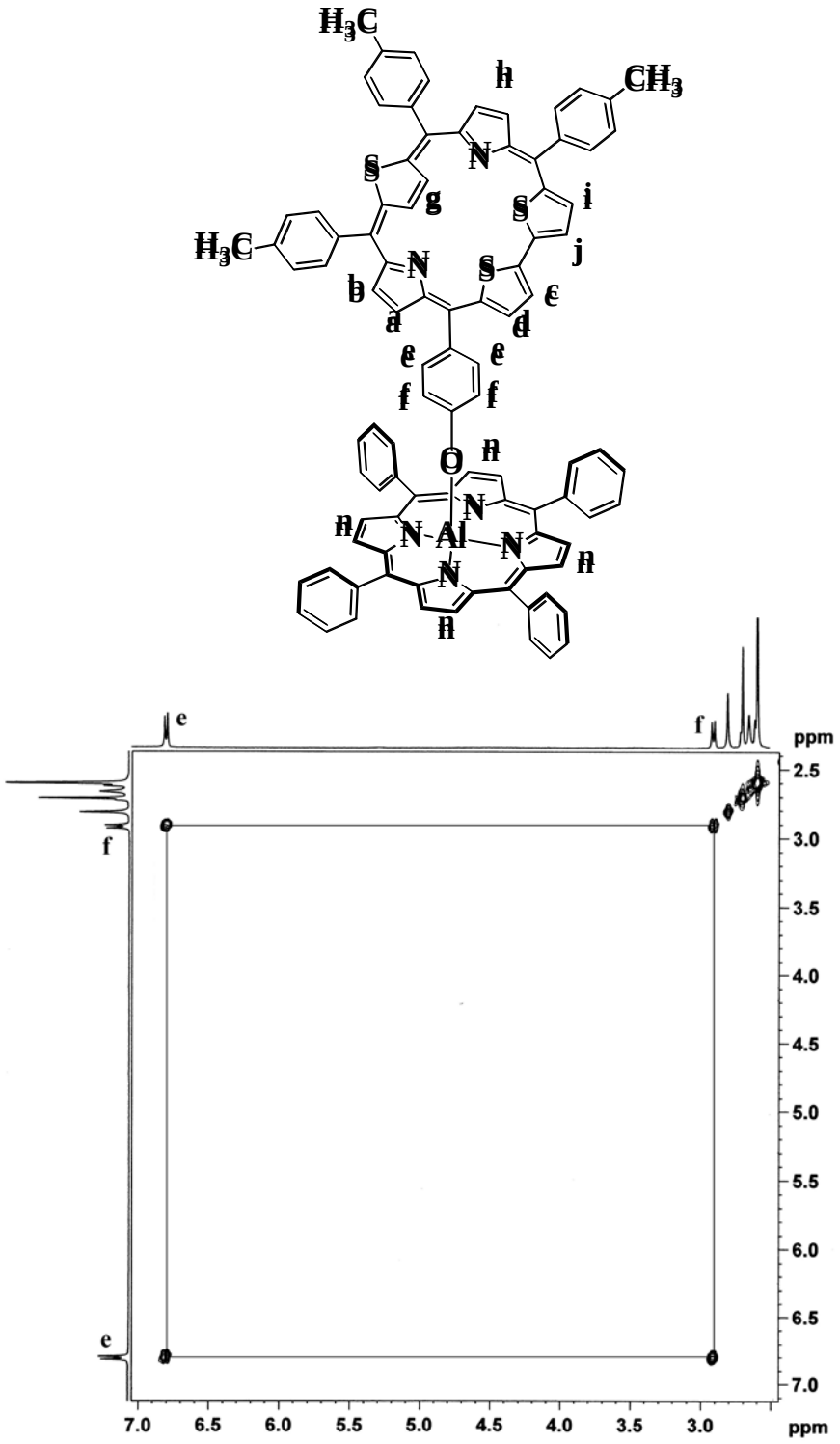


Figure S5. Partial $^{1}H–^{1}H$ COSY spectrum of dyad **3** showing the cross-peak connectivity of bridging phenoxo group recorded in $CDCl_3$ at room temperature.

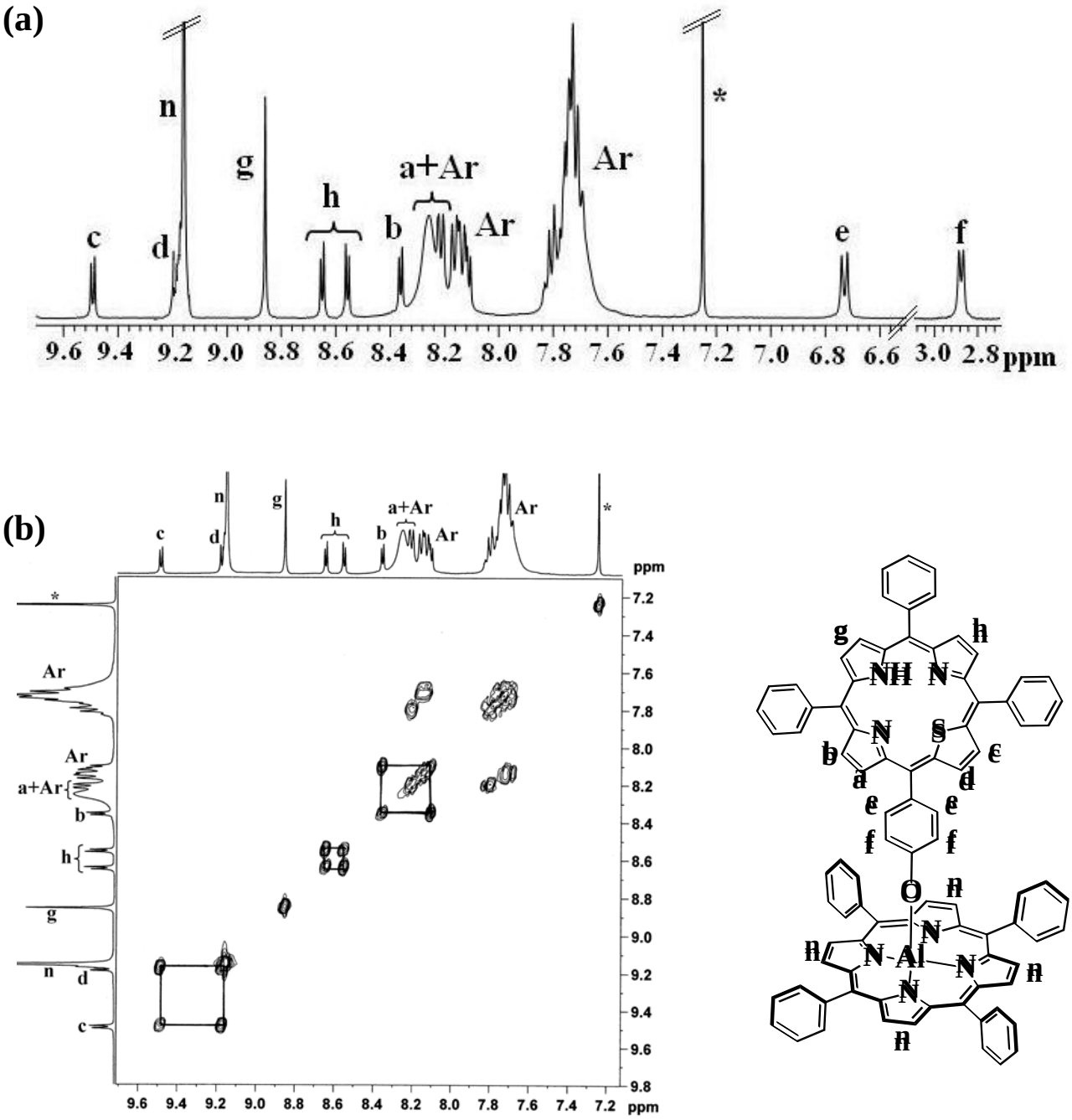


Figure S6. (a) ^{1}H NMR and (b) partial ^{1}H–^{1}H COSY spectra of dyad **1** recorded in $CDCl_3$ at room temperature.

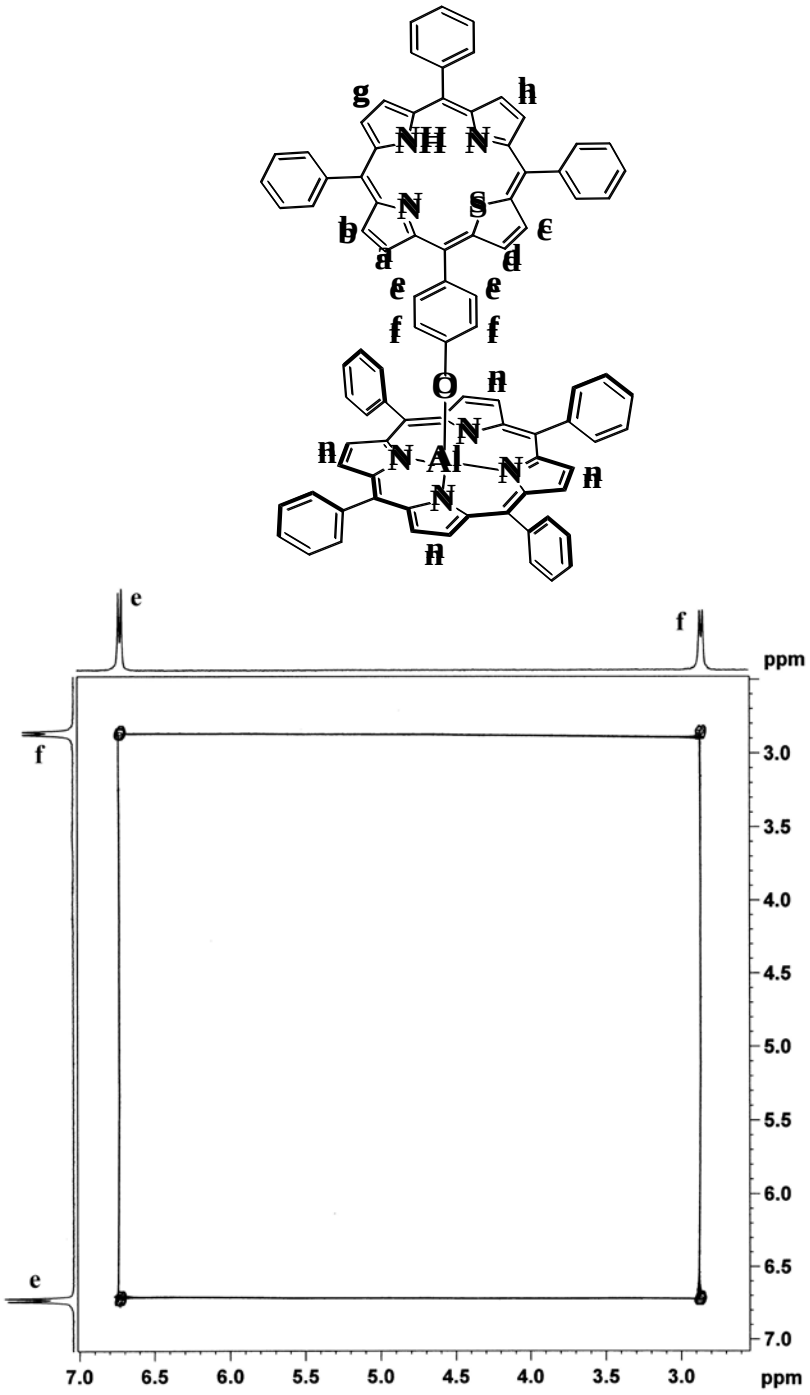


Figure S7. Partial $^{1}H–^{1}H$ COSY spectrum of dyad **1** showing the cross-peak connectivity of bridging phenoxo group recorded in $CDCl_3$ at room temperature.

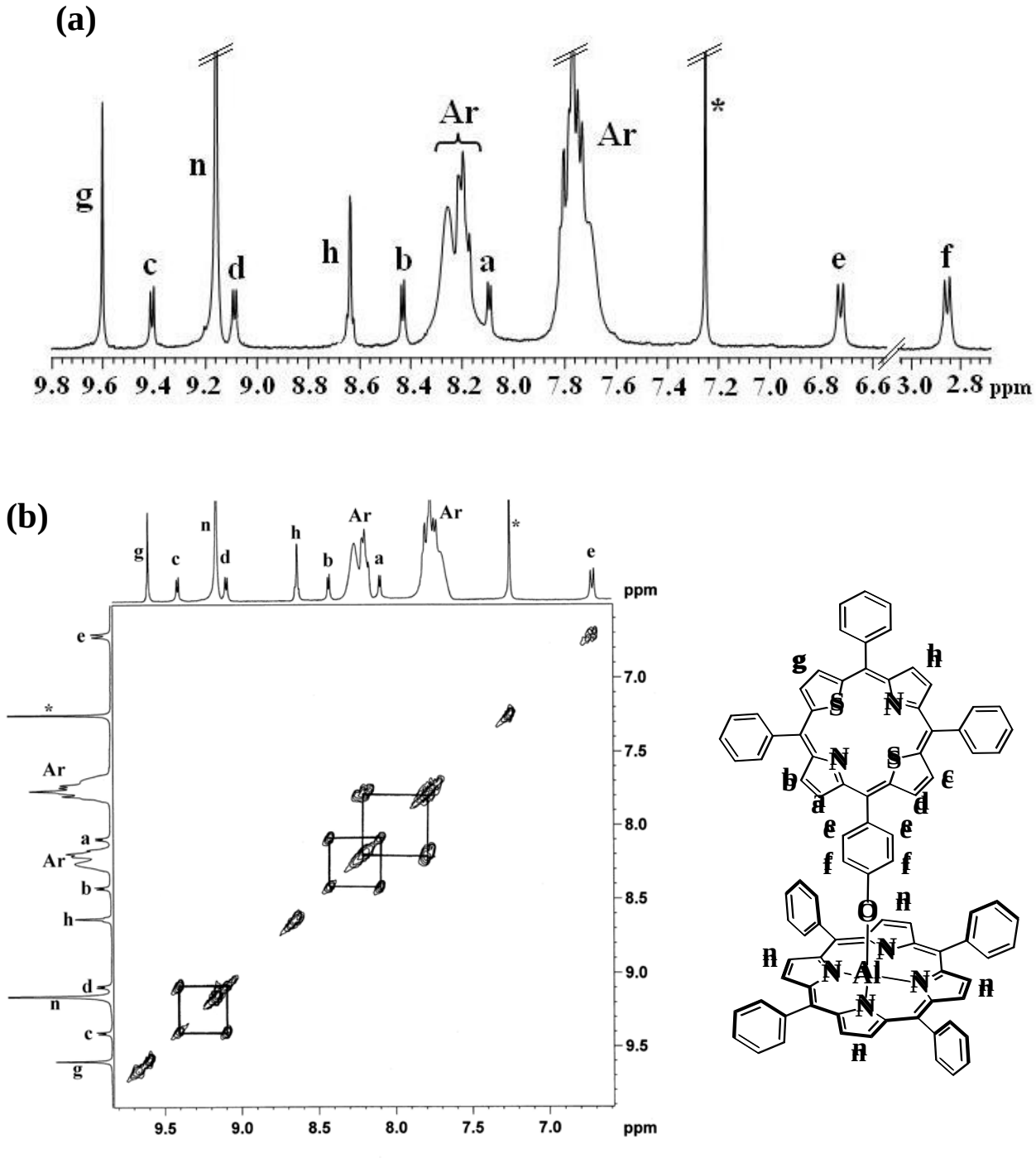


Figure S8. (a) ^{1}H NMR and (b) partial ^{1}H–^{1}H COSY spectra of dyad **2** recorded in $CDCl_3$ at room temperature.

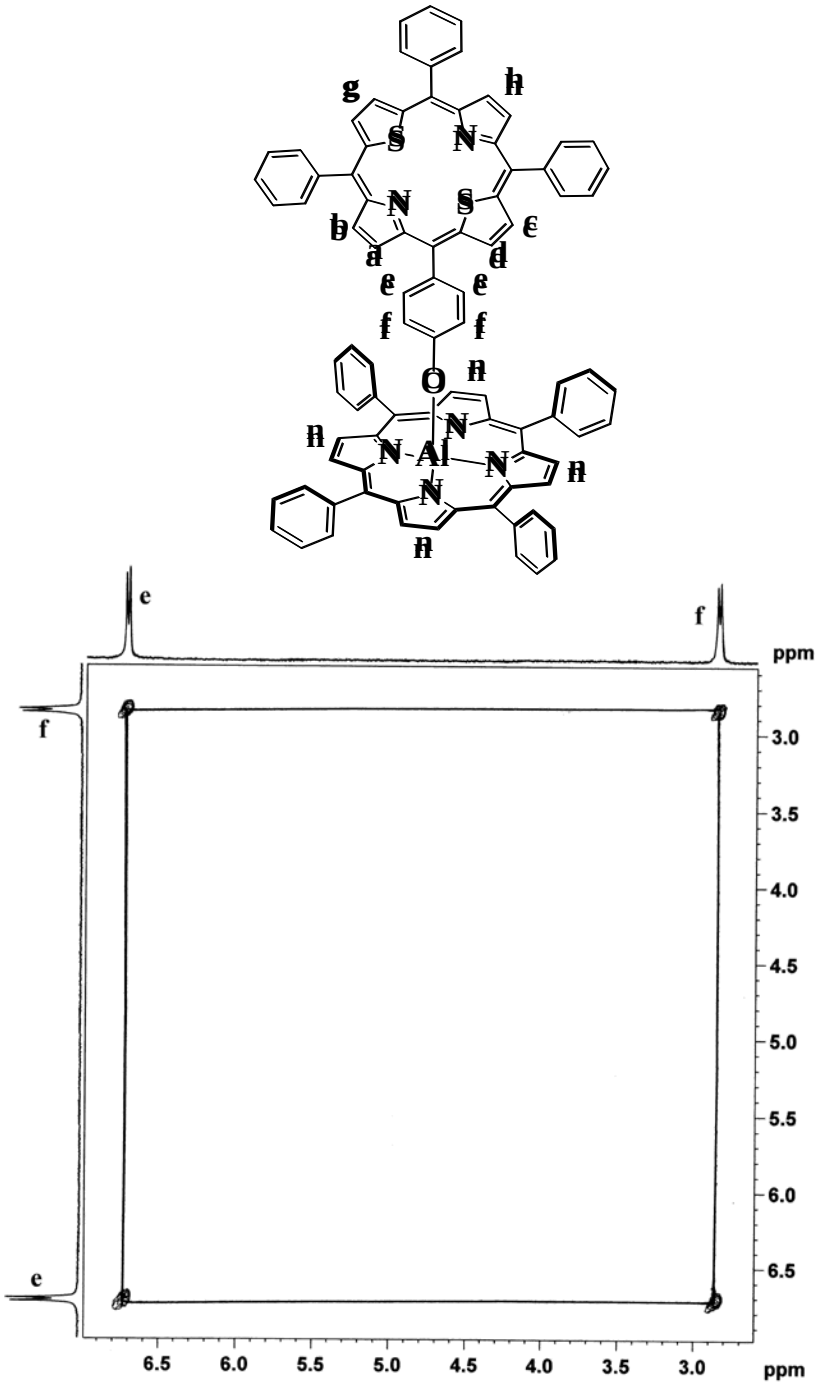


Figure S9. Partial $^{1}H–^{1}H$ COSY spectrum of dyad **2** showing the cross-peak connectivity of bridging phenoxo group recorded in $CDCl_3$ at room temperature.

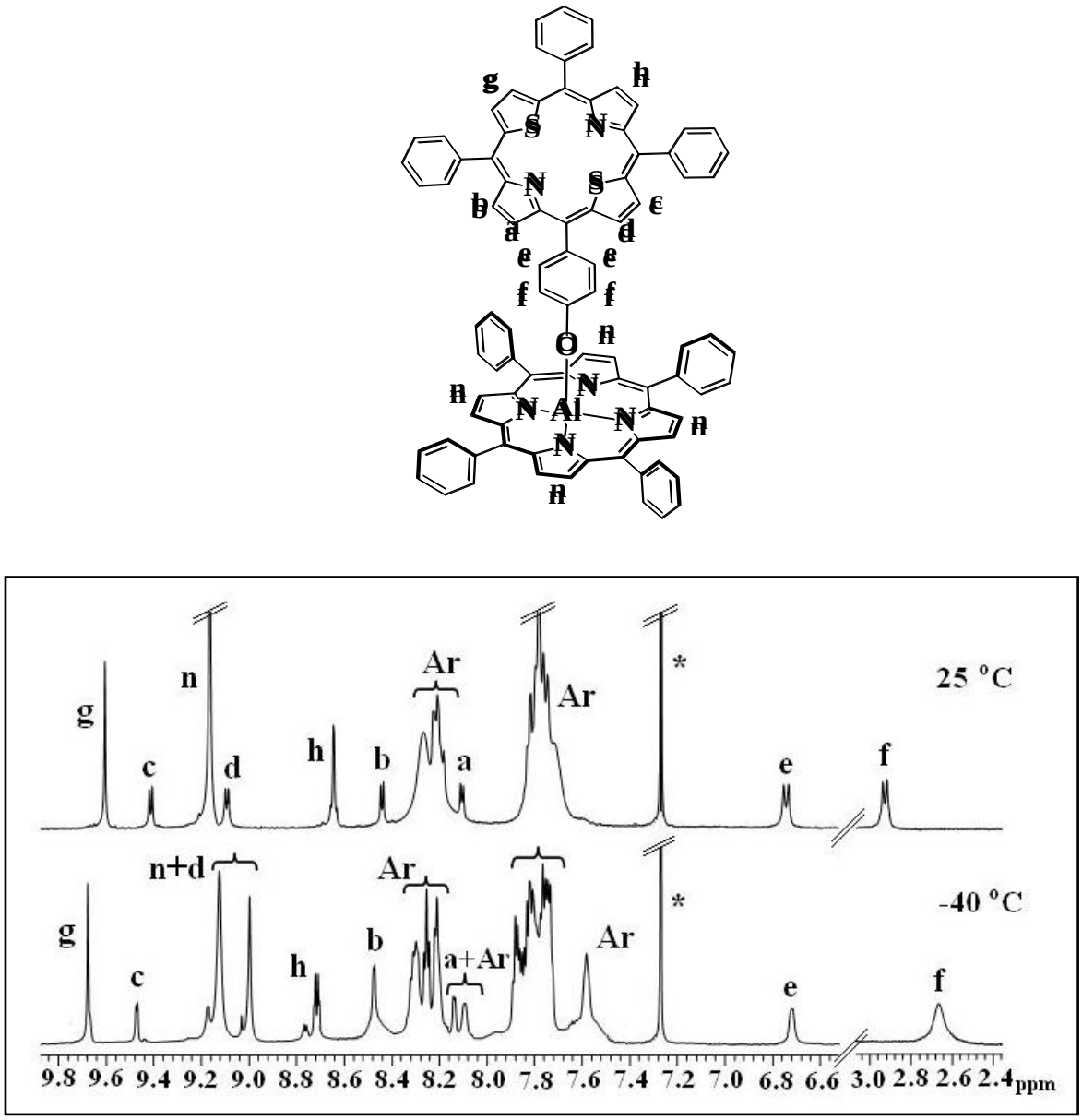


Figure S10. Comparison of ^{1}H NMR spectra of dyad **2** recorded at 25 °C and −40 °C.

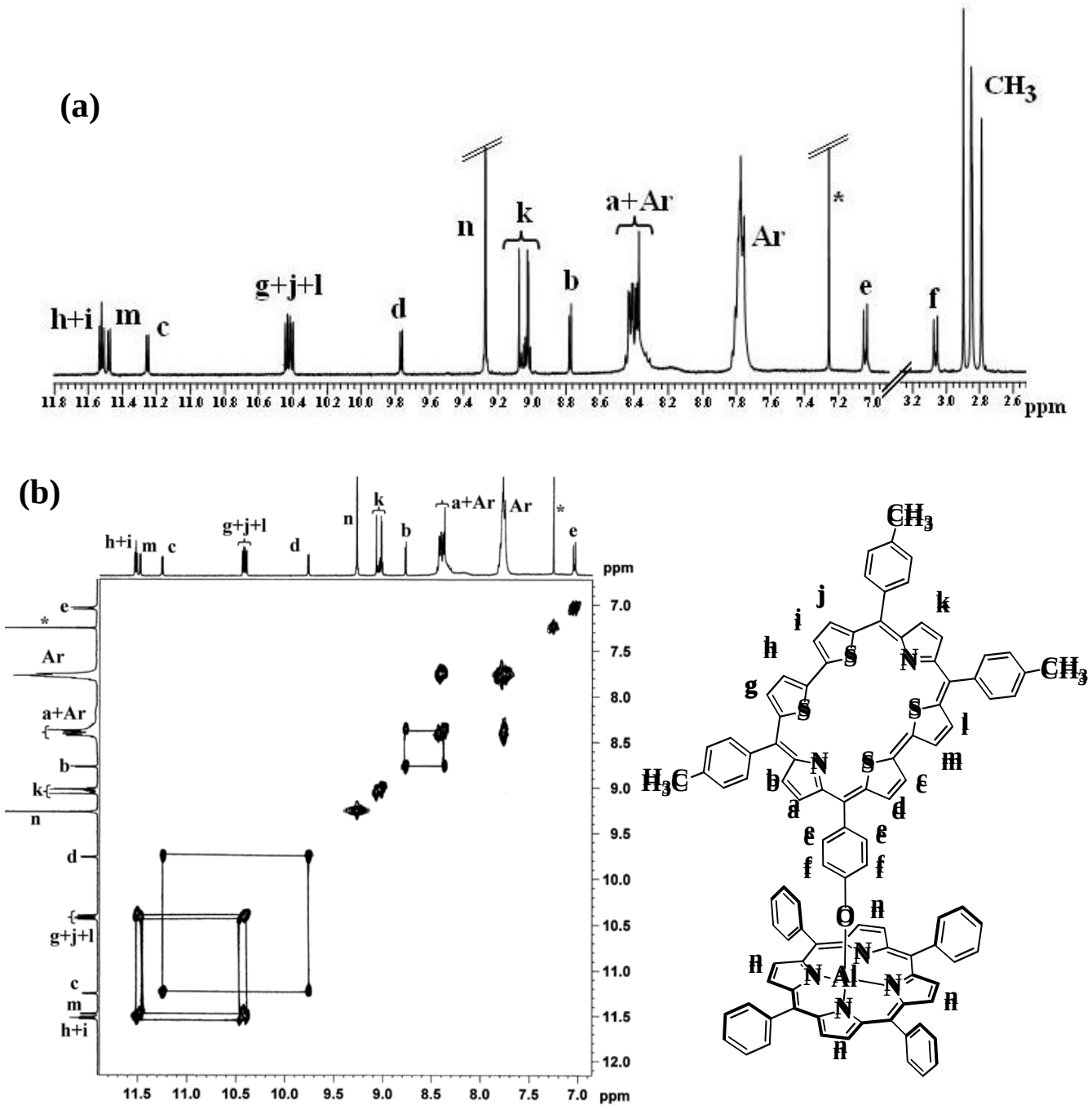


Figure S11. (a) ^{1}H NMR and (b) partial ^{1}H–^{1}H COSY spectra of dyad **4** recorded in $CDCl_3$ at room temperature.

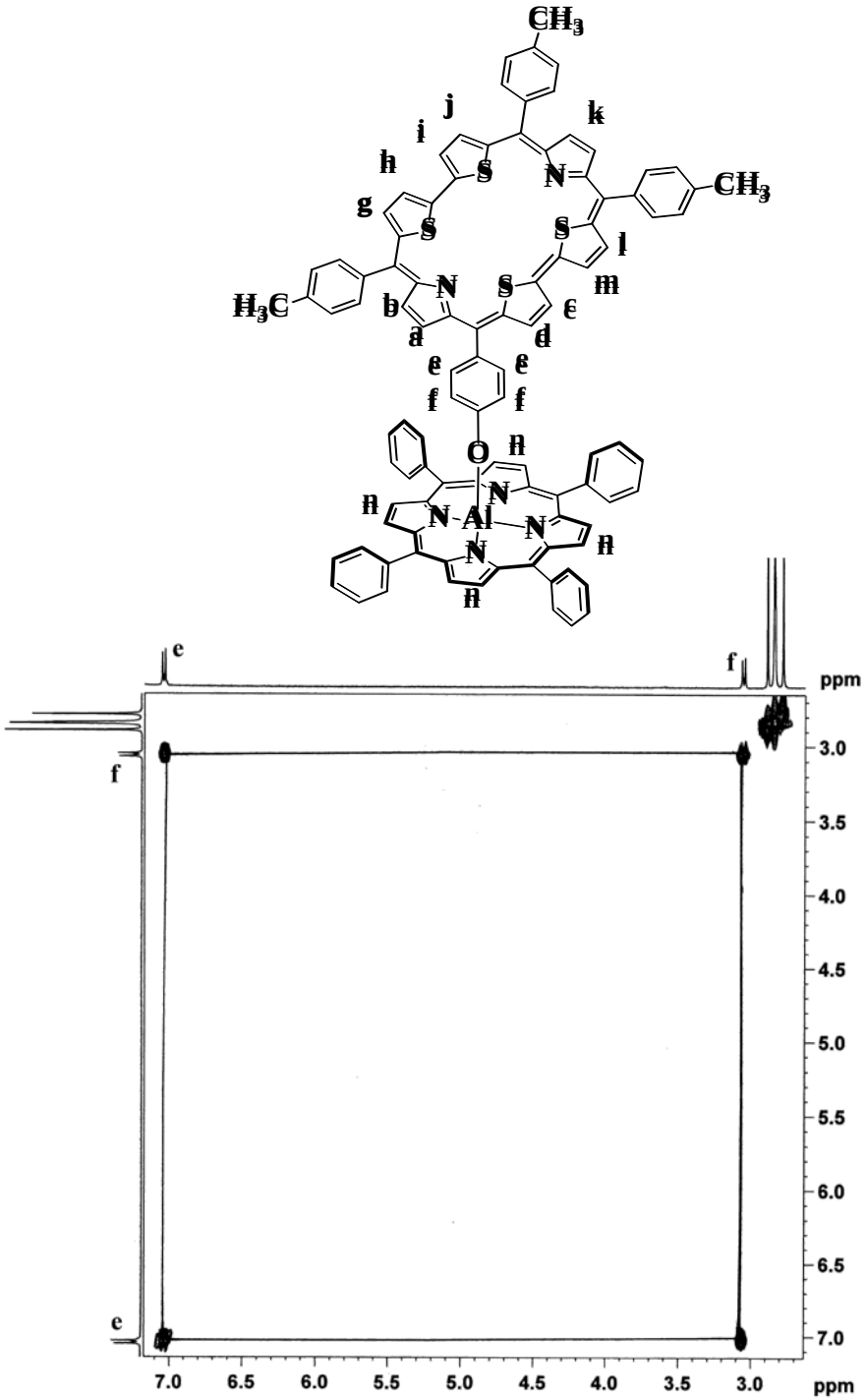


Figure S12. Partial $^{1}H–^{1}H$ COSY spectrum of dyad **4** showing the cross-peak connectivity of bridging phenoxo group recorded in $CDCl_3$ at room temperature.

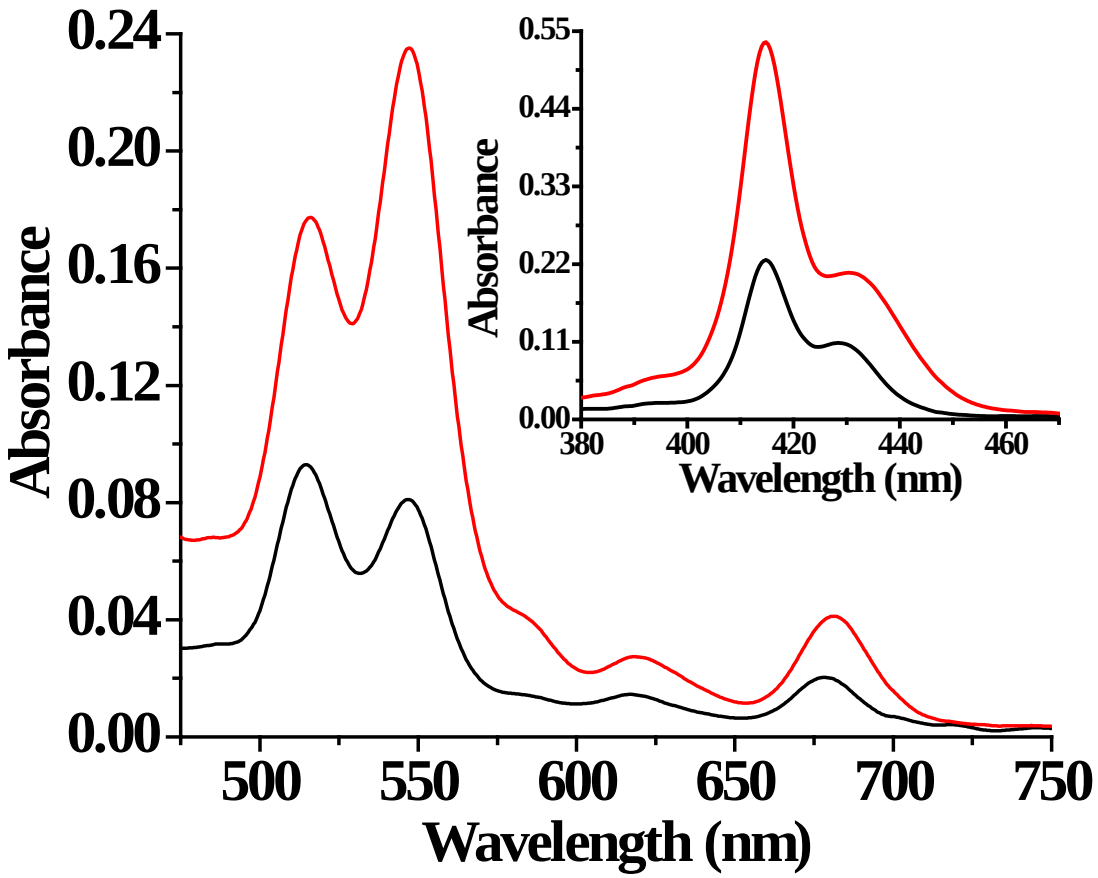


Figure S13. Q-band absorption spectra of dyad **1** (red) and 1:1 mixture (black) of corresponding constituted monomers **5** & **6** recorded in dichloromethane. The inset shows corresponding Soret band absorption spectra. Concentrations of solution used for Soret band are $1x10^{-6}$ M and for Q-band $1x10^{-5}$ M.

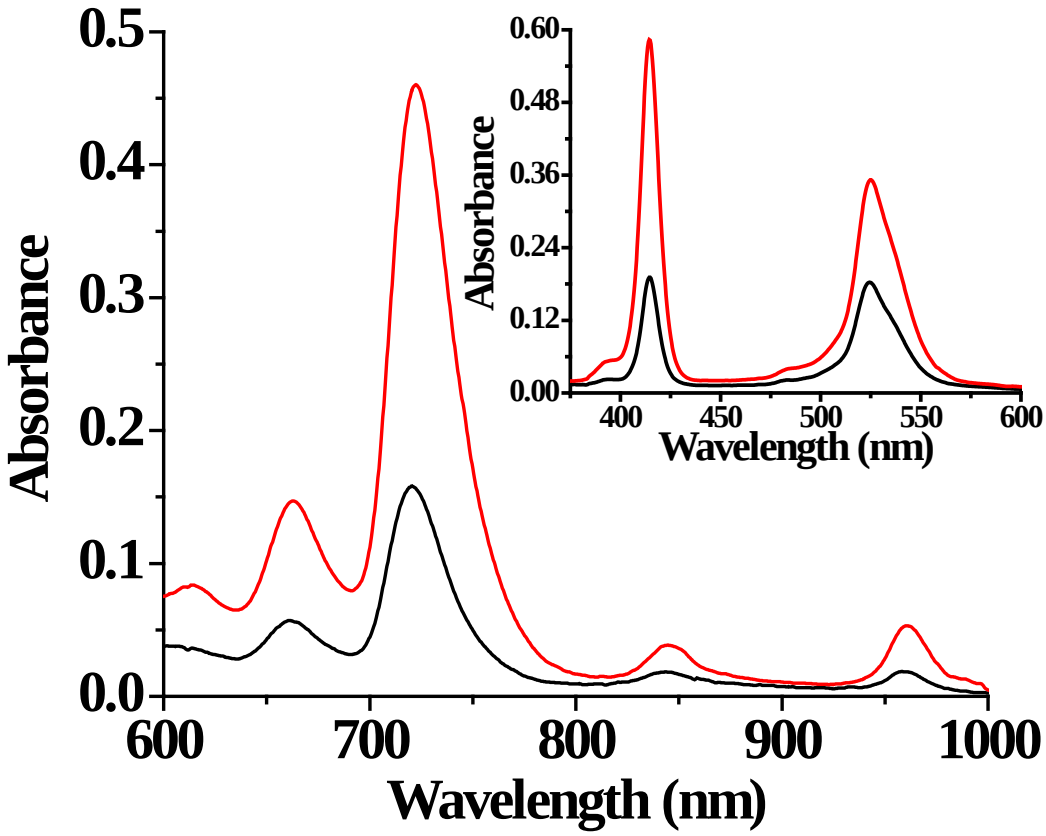


Figure S14. Q-band absorption spectra of dyad **4** (red) and 1:1 mixture (black) of corresponding constituted monomers **5** & **9** recorded in dichloromethane. The inset shows corresponding Soret band absorption spectra. Concentrations of solution used for Soret band are $1x10^{-6}$ M and for Q-band $1x10^{-5}$ M.

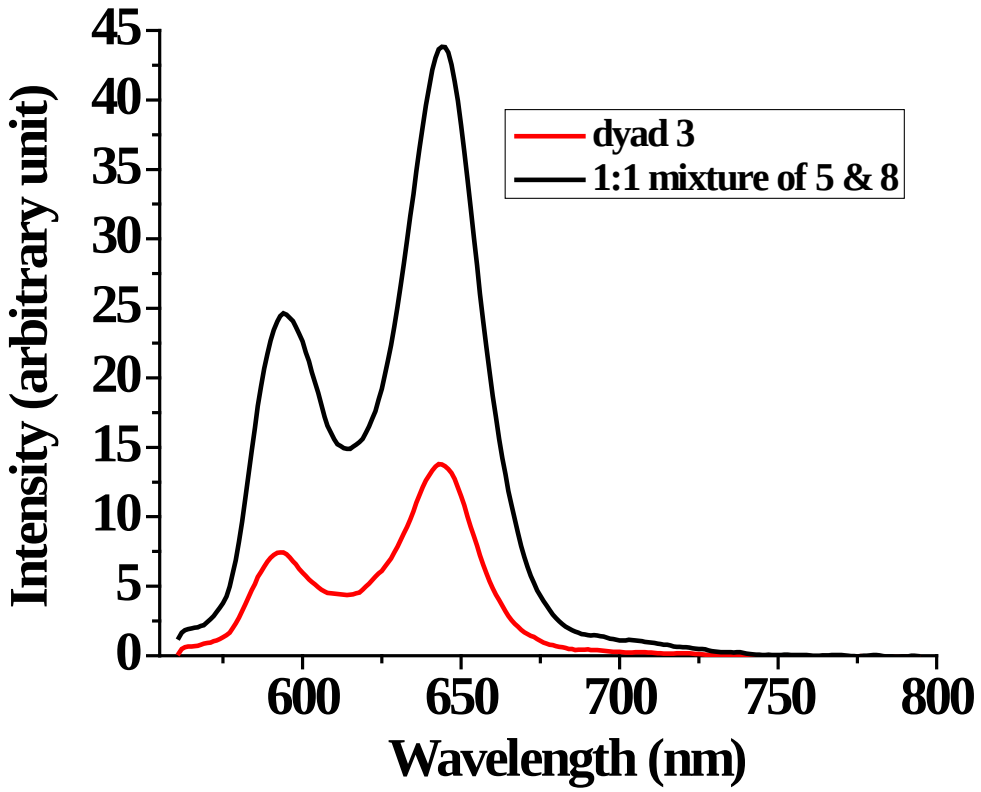


Figure S15. Fluorescence spectra of dyad **3** (red) along with 1:1 mixture (black) of corresponding constituted monomers **5** & **8** recorded in dichloromethane solvent by exciting at wavelength of 550 nm.

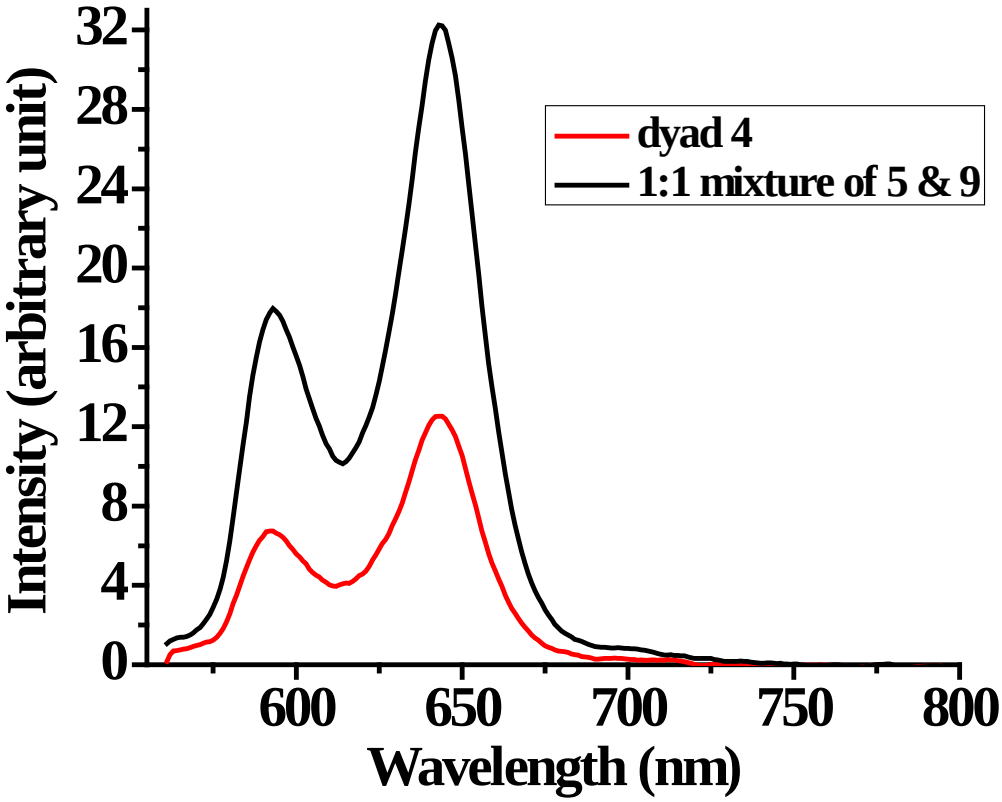


Figure S16. Fluorescence spectra of dyad **4** (red) along with 1:1 mixture (black) of corresponding constituted monomers **5** & **9** recorded in dichloromethane solvent by exciting at wavelength of 550 nm.

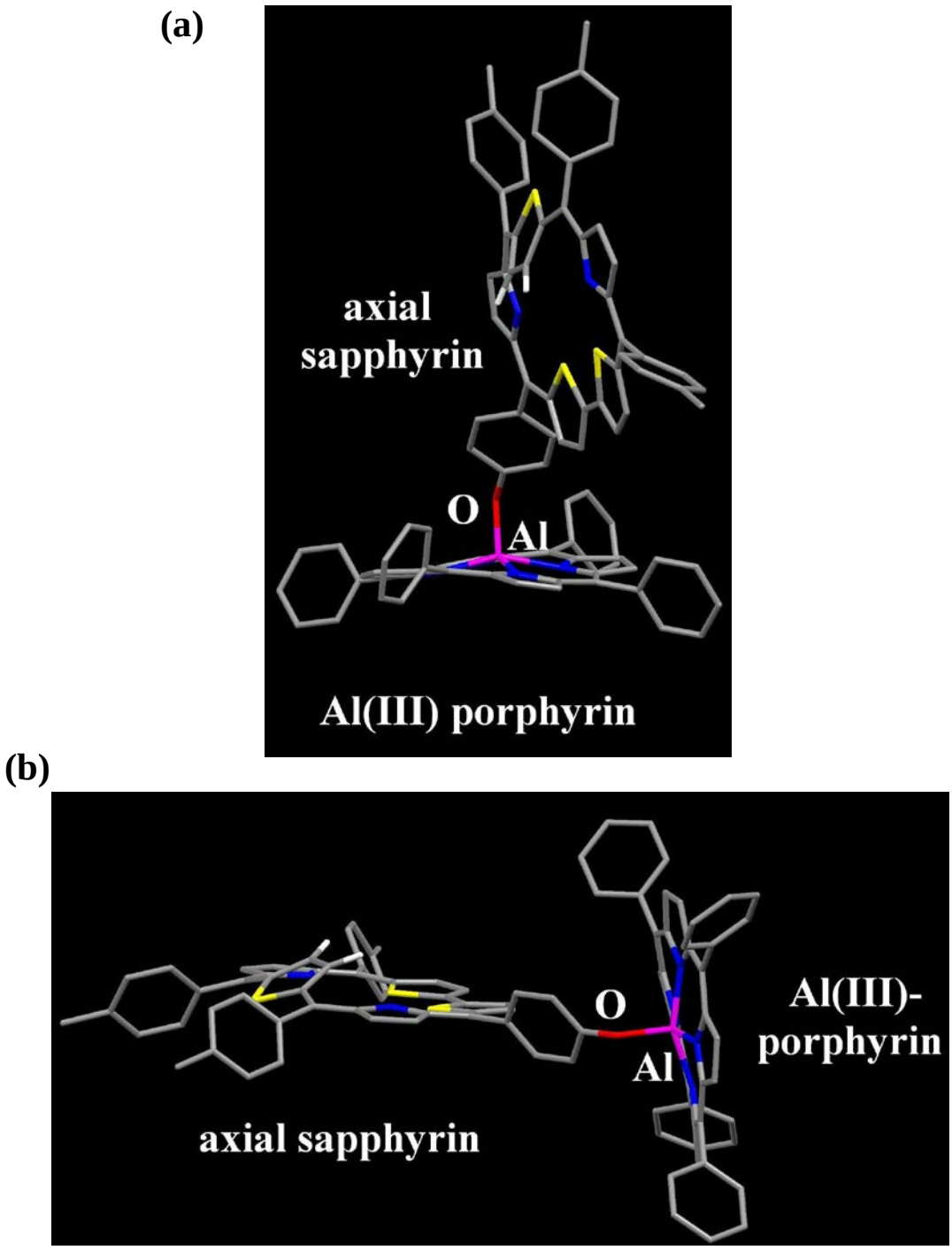


Figure S17. Fully optimized structures of dyad **3** showing the non planarity of (a) basal Al(III) porphyrin and (b) axial sapphyrin units by applying B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.

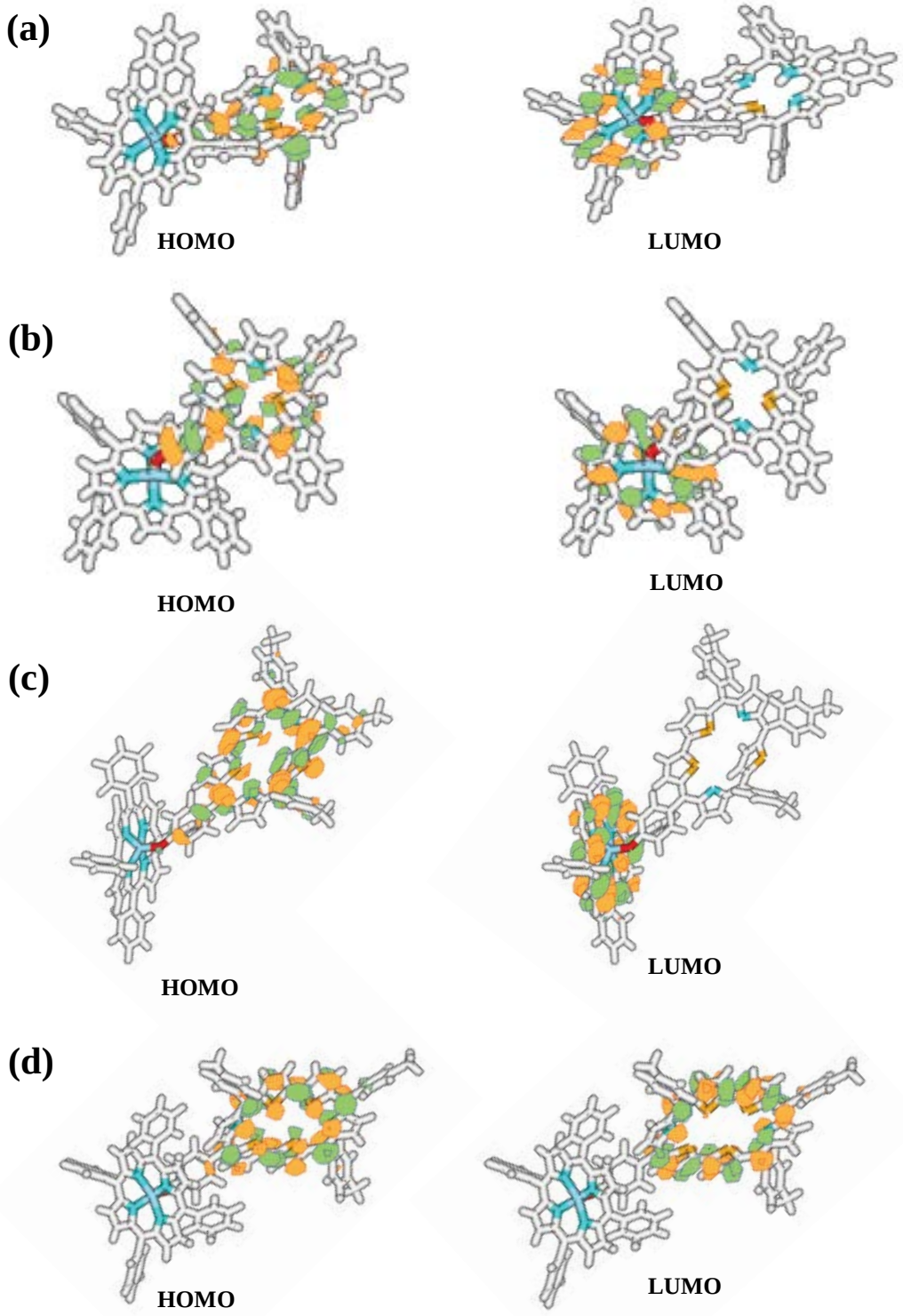
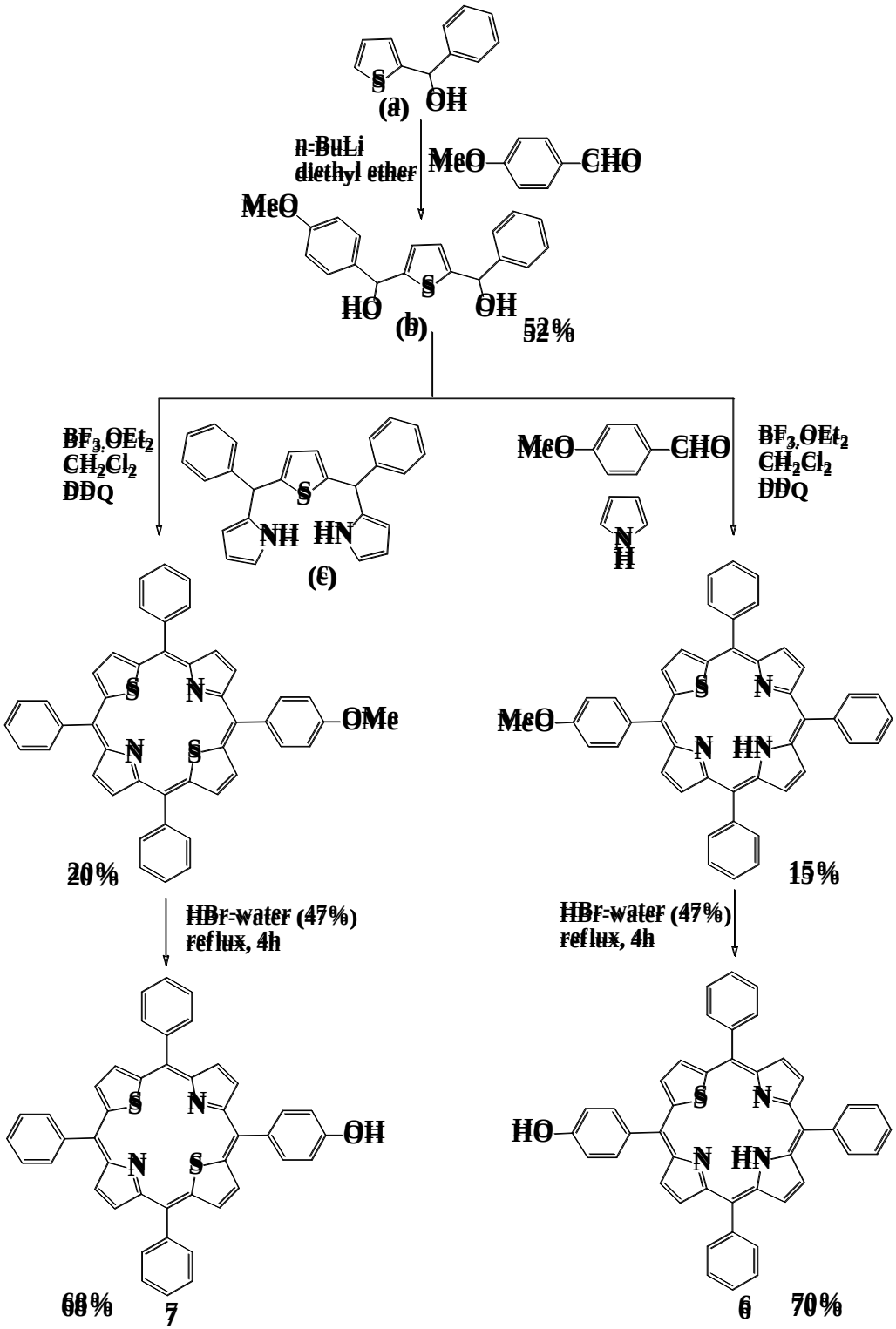
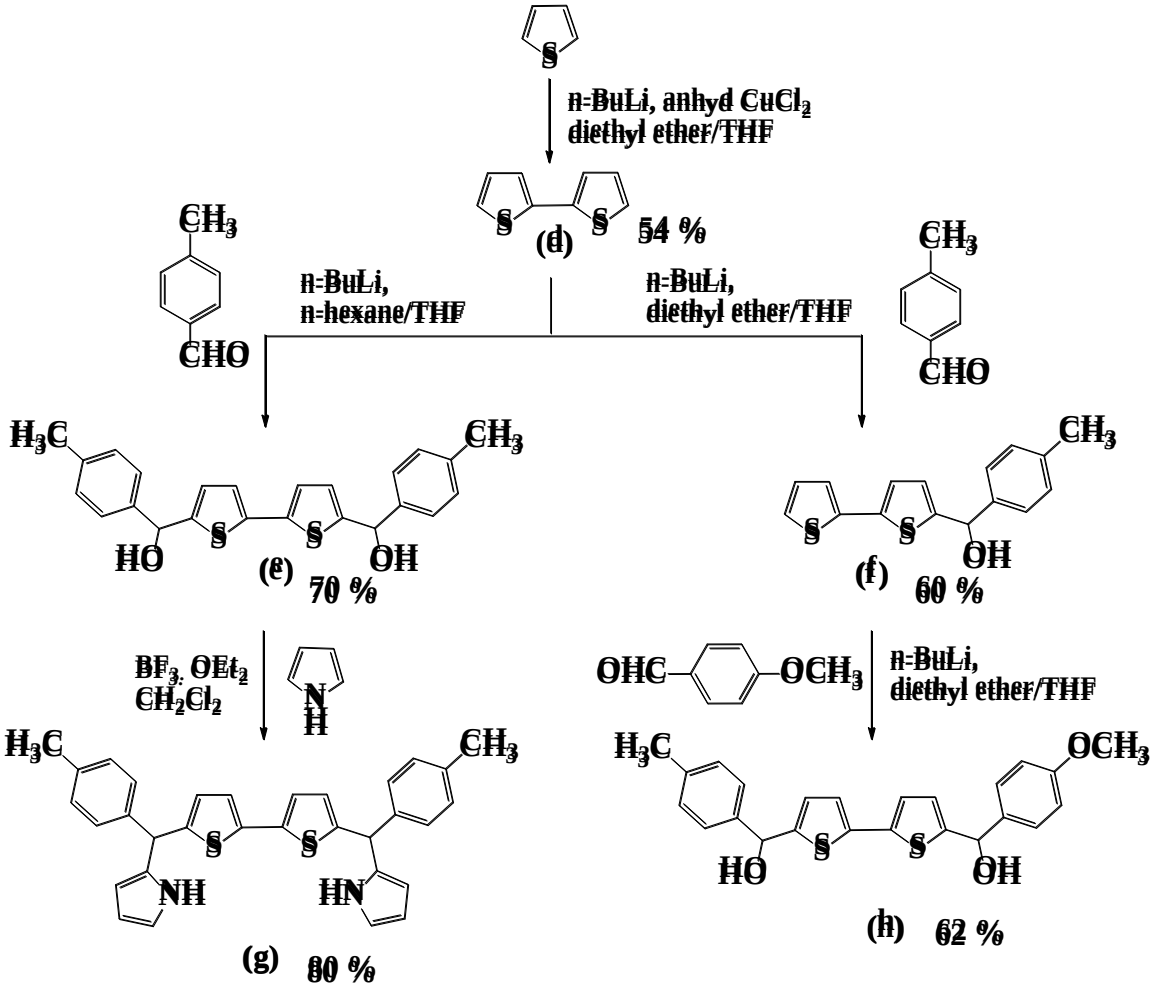


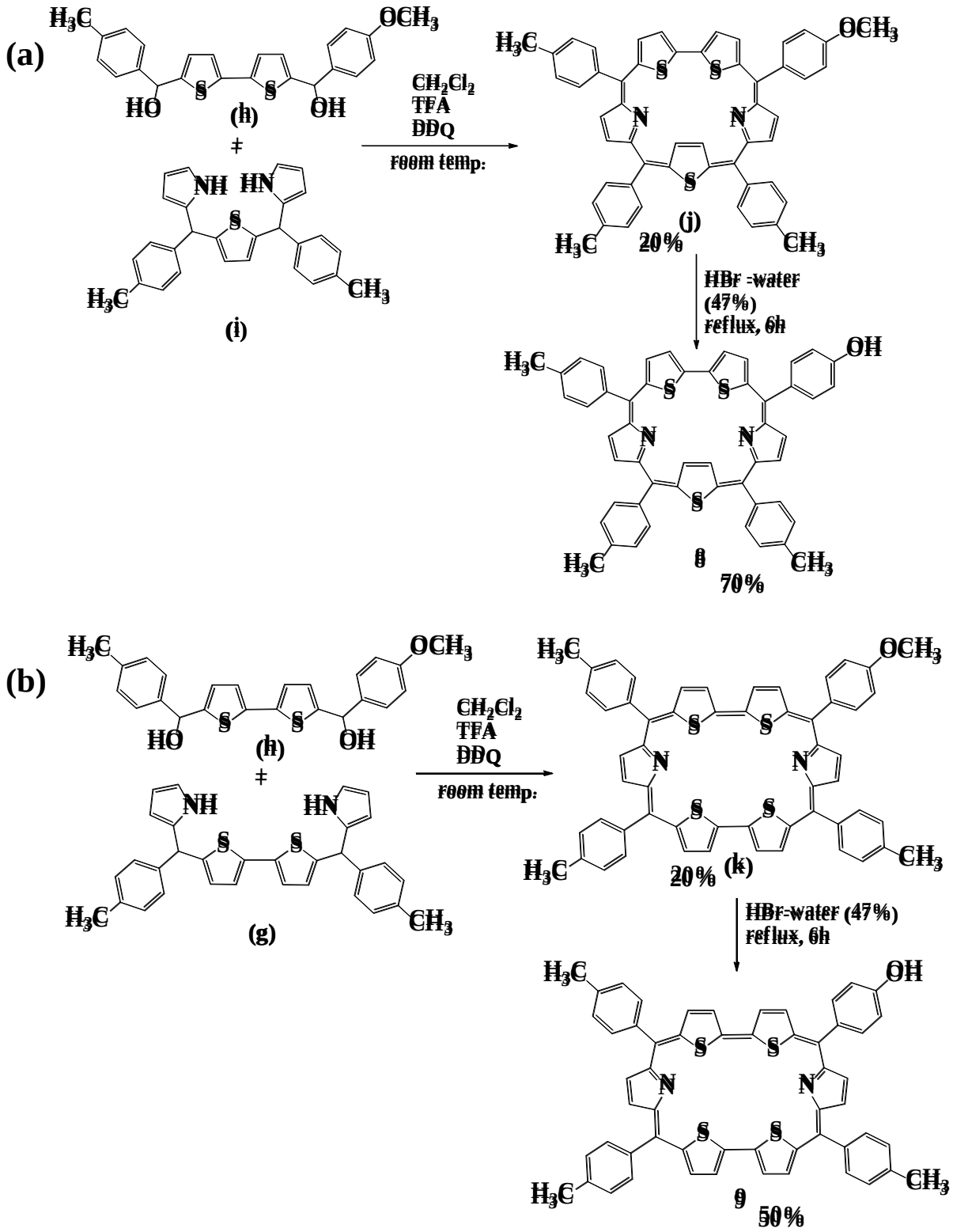
Figure S18. Pictorial presentation of frontier molecular orbitals (HOMO and LUMO) for (a) dyad **1**, (b) dyad **2**, (c) dyad **3** and (d) dyad **4**.



Scheme S1. Synthesis of mono-hydroxy thiaporphyrin building blocks **6** and **7**. Compounds **6** and **7** were synthesiszed by following the same procedure as described in reference 12a.



Scheme S2. Synthesis of building blocks required for synthesis of mono-hydroxy expanded thiaporphyrins **8** and **9**.



Scheme S3. Synthesis of mono-hydroxy expanded thiaporphyrin building blocks (a) **8** and (b) **9**. Compounds **8** and **9** were synthesiszed by following the same procedure as described in reference 12b.

Synthesis of 5-(4-Methoxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin (j):

The samples of 5-{(p-Methoxyphenyl)hydroxymethyl}-5'-{(p-tolyl)hydroxymethyl}-2,2'-bithiophene (**h**) (200 mg, 0.47 mmol) and 5,10-di(p-tolyl)-16-thia-15,17-dihydrotripyrrane (**i**) (200 mg, 0.47 mmol) were dissolved in 200 ml of dichloromethane in a 500 mL round bottom flask fitted with nitrogen bubbler. Keeping a steady positive flow of nitrogen, the condensation was initiated by the addition of TFA (35µl, 0.47 mmol) and the reaction mixture was stirred at room temperature. The progress of the reaction was followed by thin layer chromatography (TLC) and absorption spectroscopy. After 1.5 h, DDQ (107 mg, 0.49 mmol) was added and the reaction mixture was exposed to air and stirred for an additional hour at room temperature. The TLC analysis showed the formation of the desired sapphyrin along with the less polar dithiaporphyrin. The solvent was evaporated under reduced pressure and the resultant mixture was subjected to basic alumina column chromatography and the desired compound was eluted with petroleum ether/ dichloromethane (60:40). Further recrystallisation yielded 5-(4-Methoxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin **j** in 20 % yield (76 mg). mp > 300 ^{o}C, ES-MS: $C_{52}H_{38}N_2OS_3$, Calcd av. mass 803.6, obsd. m/z 802.9 $(M)^+$, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = -0.71 (s, 2H, β-thiophene), 2.62 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 4.12 (s, 3H, OCH_3), 7.39 (d, *J* = 8.5 Hz, 2H, Ar), 7.57 (d, *J* = 7.9 Hz, 4H, Ar), 7.65 (d, *J* = 7.9 Hz, 2H, Ar), 8.20 (d, *J* = 7.9 Hz, 4H, Ar), 8.24 (m, 4H, Ar), 8.54 (m, 2H, β-pyrrole), 8.65 (m, 2H, β-pyrrole), 9.77 (m, 2H, β-thiophene), 10.19 (d, *J* = 4.5 Hz, β-thiophene).

Synthesis of 5-(4-Methoxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin (k):

The samples of 5-{(*p*-Methoxyphenyl)hydroxymethyl}-5'-{(*p*-tolyl)hydroxymethyl}-2,2'-bithiophene **(h)** (200 mg, 0.47 mmol) and 20,21-(*p*-tolyl)dithiatetrapyrromethane (**g**) (238 mg, 0.47 mmol) were dissolved in 200 mL of dichloromethane in a 500 mL round bottom flask fitted with nitrogen bubbler. Keeping a steady positive flow of nitrogen, the condensation was initiated by the addition of TFA (35 µL, 0.47 mmol) and the reaction mixture was stirred at room temperature. The progress of the reaction was followed by thin layer chromatography (TLC) and absorption spectroscopy. After 1.5 h, DDQ (107 mg, 0.49 mmol) was added and the reaction mixture was exposed to air and stirred for an

additional hour at room temperature. The TLC analysis showed the formation of the desired rubyrin along with the less polar tetratolyl tetrathiarubyrin. The solvent was evaporated under reduced pressure and the resultant mixture was subjected to basic alumina column chromatography and the desired compound was eluted with pet ether/ dichloromethane (60:40). Further recrystallisation yielded 5-(4-Methoxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin **k** in 20 % yield (84 mg). mp > 300 ^{o}C, ES-MS: $C_{56}H_{40}N_2OS_4$, Calcd av. mass 885.1, obsd. m/z 885.1 $(M)^+$, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.85 (s, 9H, CH_3), 4.22 (s, 3H, OCH_3), 7.51 (d, *J* = 8.2 Hz, 2H, Ar), 7.77 (d, *J* = 7.9 Hz, 6H, Ar), 8.43 (d, *J* = 7.0 Hz, 6H, Ar), 8.50 (d, *J* = 8.2 Hz, 2H, Ar), 9.04 (s, 4H, β-pyrrole), 10.42-10.18 (m, 4H, β-thiophene), 11.56-11.59 (m, 4H, β-thiophene).

General synthesis of 5-(4-Hydroxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin (8) and 5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin (9).

The sample of methoxy derivative of sapphyrin **j** / rubyrin **k** (100 mg) was refluxed in 40 mL of HBr-water and the reaction progress was monitored by TLC. The reaction mixture was extracted with dichloromethane and washed several times with water and dilute ammonia solution (25% v/v). The organic layer was evaporated under reduced pressure and subjected to basic alumina column chromatography to afford 5-(4-Hydroxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin **8** and 5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin **9** in 70% and 50% yields respectively.

5-(4-Hydroxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin (8):

M. P. > 300 ^{o}C, ES-MS: $C_{51}H_{36}N_2OS_3$, Calcd av. mass 789.3, Obsd. m/z 790.8 $(M+H)^+$, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = -0.73 (s, 2H, β-thiophene), 2.61 (s, 6H, CH_3), 2.72 (s, 3H, CH_3), 7.17 (d, *J* = 8.2 Hz, 2H, Ar), 7.57 (d, *J* = 6.7 Hz, 4H, Ar), 7.66 (d, *J* = 7.9 Hz, 2H, Ar), 8.08 (d, *J* = 8.5 Hz, 2H, Ar), 8.20 (d, *J* = 7.9 Hz, 2H, Ar), 8.25-8.28 (M, 4H, Ar), 8.52-8.55 (m, 2H, β-pyrrole), 8.60 (d, *J* = 4.2 Hz, 1H, β-pyrrole), 8.64 (d, *J* =

4.2 Hz, 1H, β-pyrrole), 9.70 (d, *J* = 4.5 Hz, 1H, β-thiophene), 9.76 (d, *J* = 4.5 Hz, 1H, β-thiophene), 10.14-10.16 (m, 2H, β-thiophene).

5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin (9):

M. P. > 300 ^{o}C, ES-MS: $C_{55}H_{38}N_2OS_4$, Calcd av. mass 871.1, Obsd. m/z 872.3 $(M+H)^+$, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.85 (s, 9H, CH_3), 7.18 (d, *J* = 8.0 Hz, 2H, Ar), 7.77 (d, *J* = 7.9 Hz, 6H, Ar), 8.39 (d, *J* = 8.0 Hz, 2H, Ar), 8.43 (d, *J* = 7.9 Hz, 6H, Ar), 9.04-9.06 (m, 4H, β-pyrrole), 10.46-10.48 (m, 4H, β-thiophene), 11.57 (d, *J* = 4.8 Hz, 4H, β-thiophene).