A photodimerizable ditopic ligand

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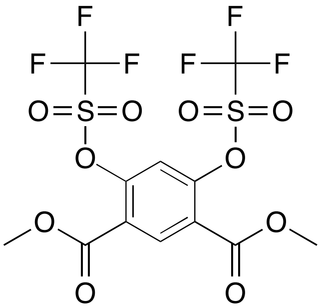
General Procedures

NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. Mass spectra were recorded at the UCSD Chemistry and Biochemistry Mass Spectrometry Facility, utilizing either a LCQDECA (Finnigan) ESI with a quadrapole ion trap or a MAT900XL (ThermoFinnigan) FAB double focusing mass spectrometer. UV-Vis spectra were recorded on either a Hewlett Packard 8452A. Fluorescence spectra were recorded on a Perkin-Elmer LS50B Luminescence Spectrometer. Unless otherwise specified, materials obtained from commercial suppliers were used without further purification. Anhydrous pyridine and acetonitrile were obtained from Fluka. Anhydrous dioxane and triethylamine were obtained from Acros. Anhydrous dichloromethane and tetrahydrofuran were obtained using a two-column purification system (Glasscontour System, Irvine, CA). NMR solvents were purchased from Cambridge Isotope Laboratories (Andover, MA).

Synthetic Procedures and Analytical Data (^{1}H-NMR, ^{13}C-NMR, MS, UV-Vis).

Compound 4 : dimethyl 4,6-bis(trifluoromethylsulfonyloxy)isophthalate.



To a solution of dimethyl 4,6-dihydroxyisophthalate (1.00 g, 4.4 mmol) in 75 ml of a mixture of CH_2Cl_2/pyridine (70/30) at 0 °C, was slowly added 1.8 ml (10.6 mmol) of triflic anhydride. The reaction mixture was allowed to reach room temperature and was stirred for 40 minutes. It was then washed with 250 ml of 5 % HCl. The organic phase was dried over Na_2SO_4 and the solvent evaporated, affording 1.715 g of compound **4** (3.5 mmol; 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 7.26 (s, 1H), 4.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 150.8, 137.3, 124.9, 120.4, 118.6, 53.6

Fig S.1. ^{1}H NMR Spectrum of Compound 4

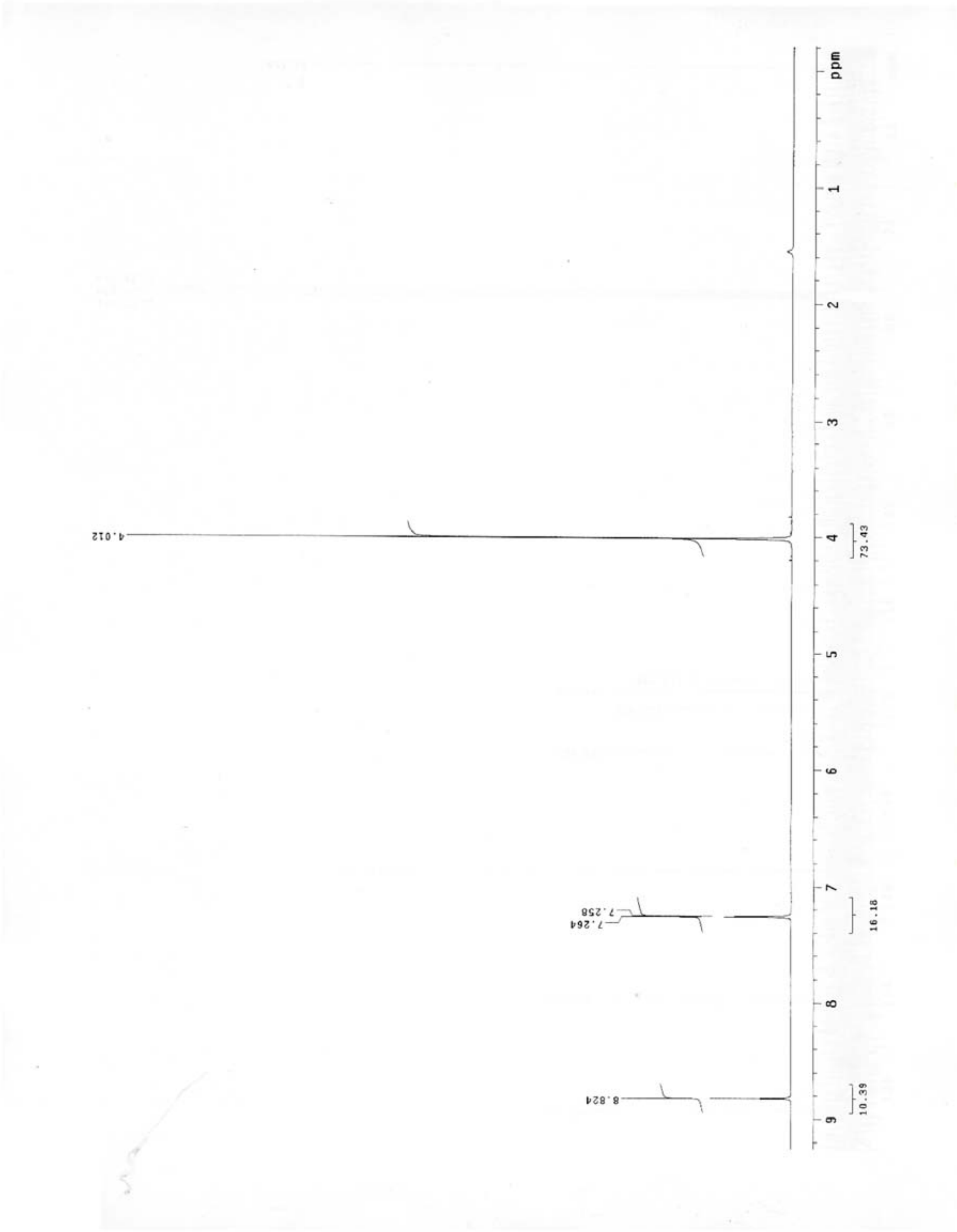
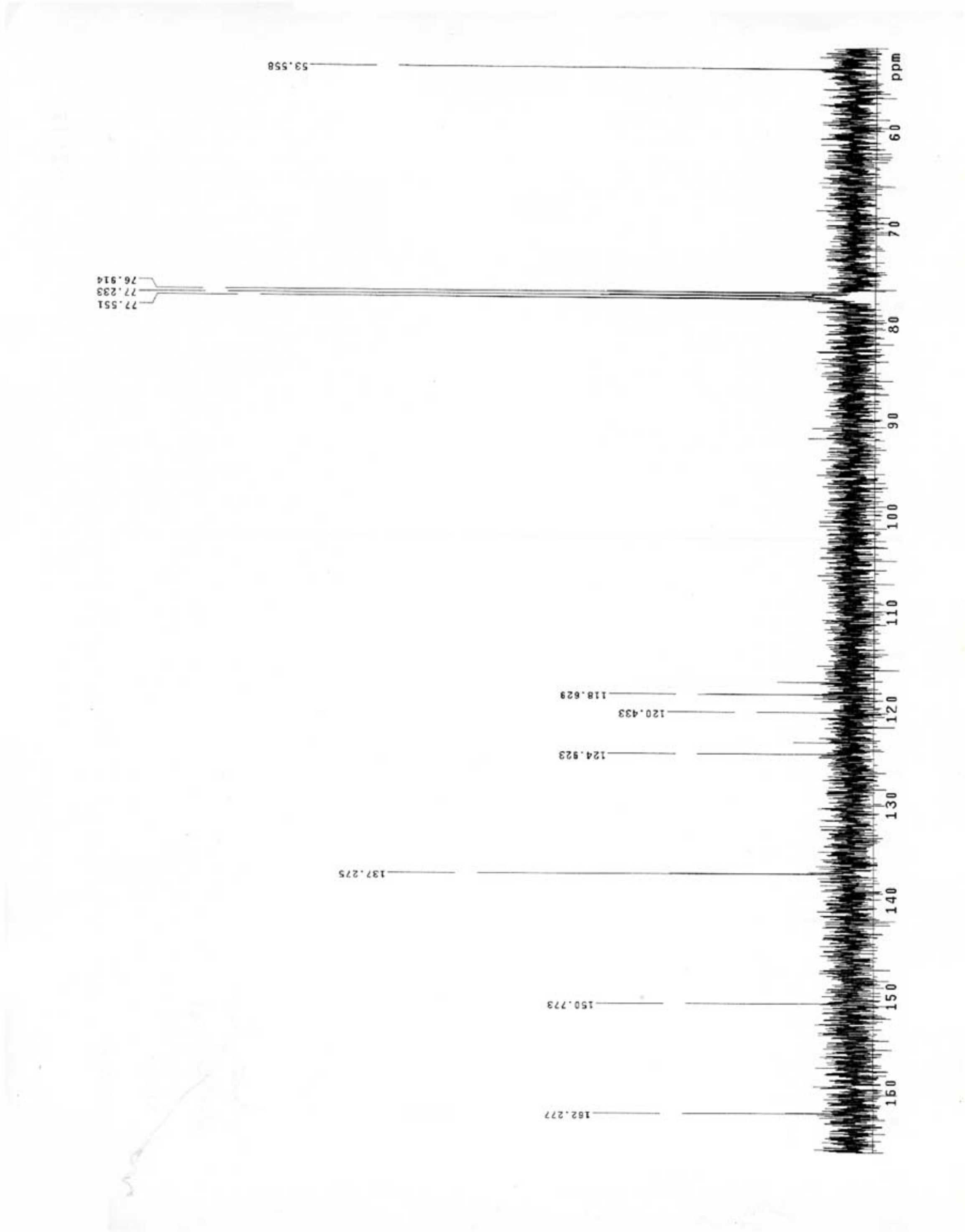
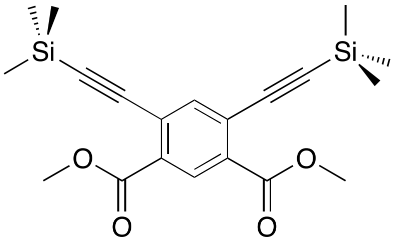


Fig S.2. ^{13}C NMR Spectrum of compound 4



Compound 5 : dimethyl 4,6-bis(2-(trimethylsilyl)ethynyl)isophthalate.



A degassed solution of **4** (915 mg, 1.86 mmol) in a 1/1 mixture of dry THF and dry triethylamine (7.5 ml) was cannulated into a pressure tube containing Pd(dppf)Cl_2 (152 mg, 0.186 mmol) and CuI (36 mg, 0.186 mmol). To this solution was cannulated a solution of trimethylsilyl acetylene (2.65 ml, 18.6 mmol) in a 1/1 mixture of dry THF and dry triethylamine (7.5 ml). The pressure tube was sealed and stirred at 45 °C overnight. The reaction was then cooled down to room temperature and the solvents are evaporated. The crude product was taken up in a CH_2Cl_2/H_2O mixture, and the organic phase washed 3 times with water. The organic phase was dried over Na_2SO_4 and the solvent evaporated. Column chromatography on SiO_2 (AcOEt/Hexanes 20%) afforded 0.635 mg (1.64 mmol; 88% yield) of **5** as a white powder. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 7.78 (s, 1H), 3.92 (s, 6H), 0.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 140.7, 132.9, 131.5, 126.8, 104.1, 101.9, 52.5, -0.1; MS *m/z* calculated for $C_{20}H_{27}O_4Si_2$ $[M+H]^+$ 387.14, found 387.03.

Fig S.3. ^{1}H NMR Spectrum of Compound 5

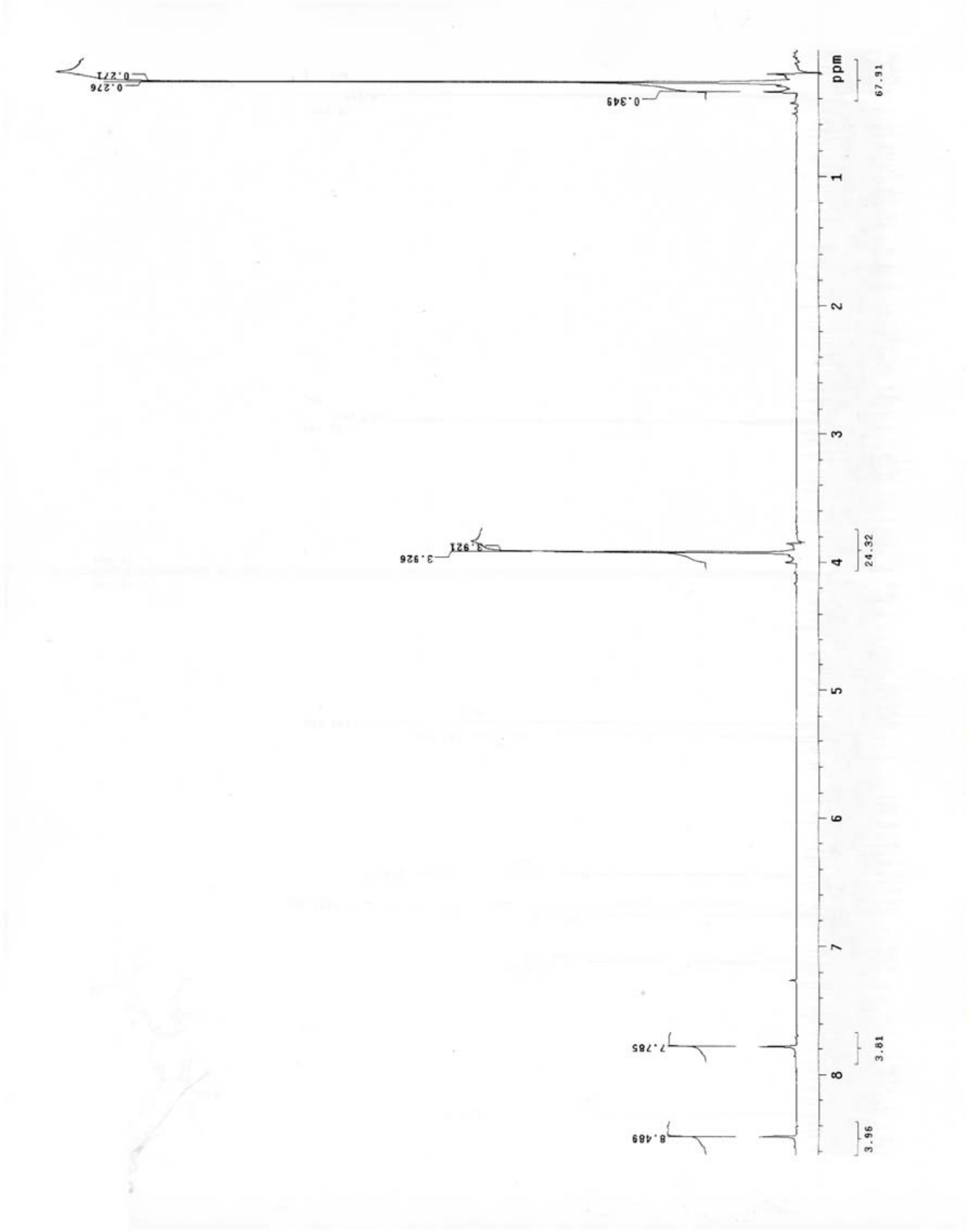
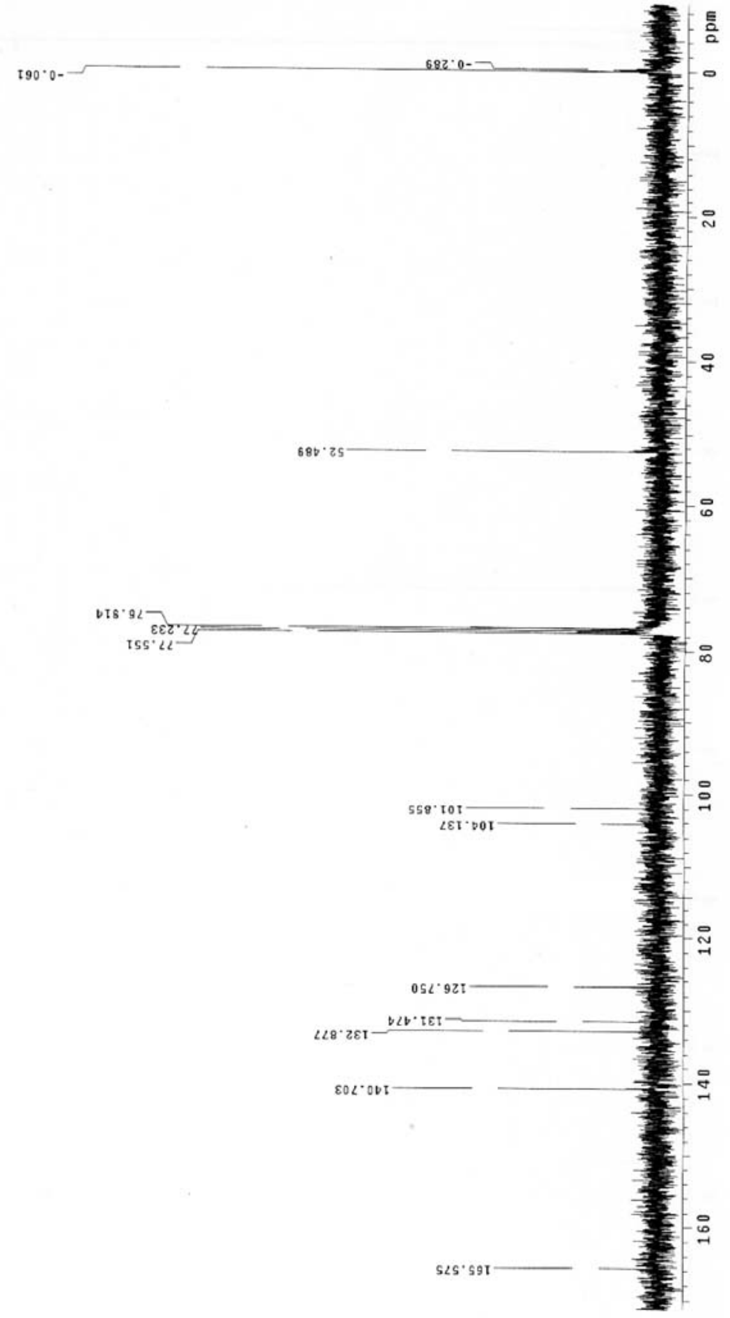
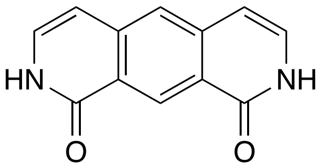


Fig S.4. ^{13}C NMR Spectrum of Compound 5



Compound 6 : 1,8-dihydroxy-2,7-diazaanthracene.



Ammonia was bubbled through a suspension of **5** (4.475 g, 11.6 mmol) in absolute ethanol (30 ml) at 0 °C in a pressure tube. Once saturated, the pressure tube was sealed and the reaction mixture stirred at 140 °C overnight. The reaction mixture was then cooled down to 0 °C and the pressure tube carefully opened. The remaining ammonia was removed by bubbling air through the suspension. The reaction mixture was filtered and the precipitate washed with cold methanol. The solid was then dried under vacuum affording 1.375 g of product **6** (6.5 mmol, 56% yield) as a yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.01 (s, 1H), 7.79 (s, 1H), 7.22 (d, J = 7.2 Hz, 2H), 6,55 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5, 140.7, 131.6, 128.0, 125.0, 122.0, 104.7; ESI-MS m/z calculated for $C_{12}H_9N_2O_2$ $[M+H]^+$ 213.22, found 213.07.

Fig S.5. ^{1}H NMR Spectrum of Compound 6

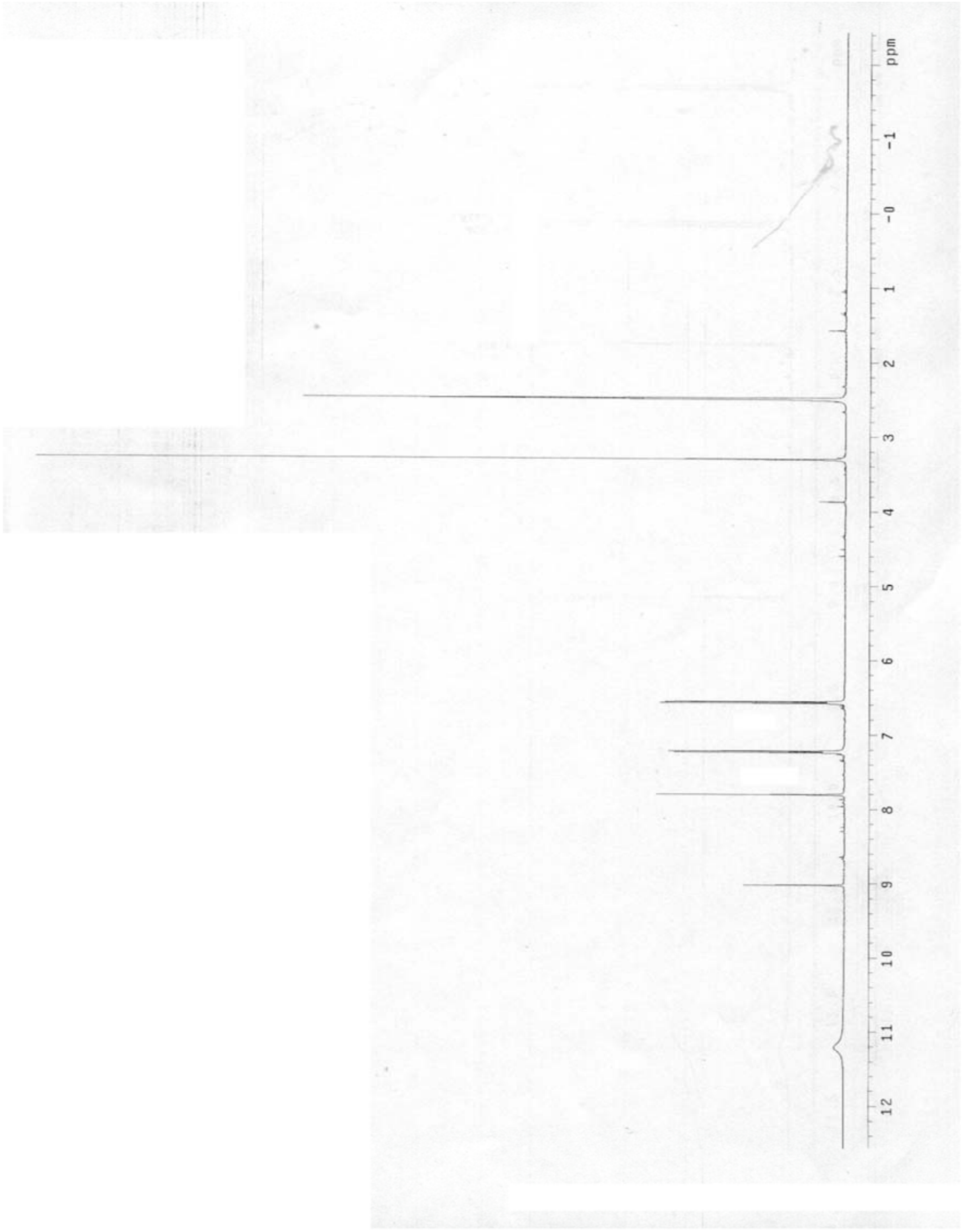
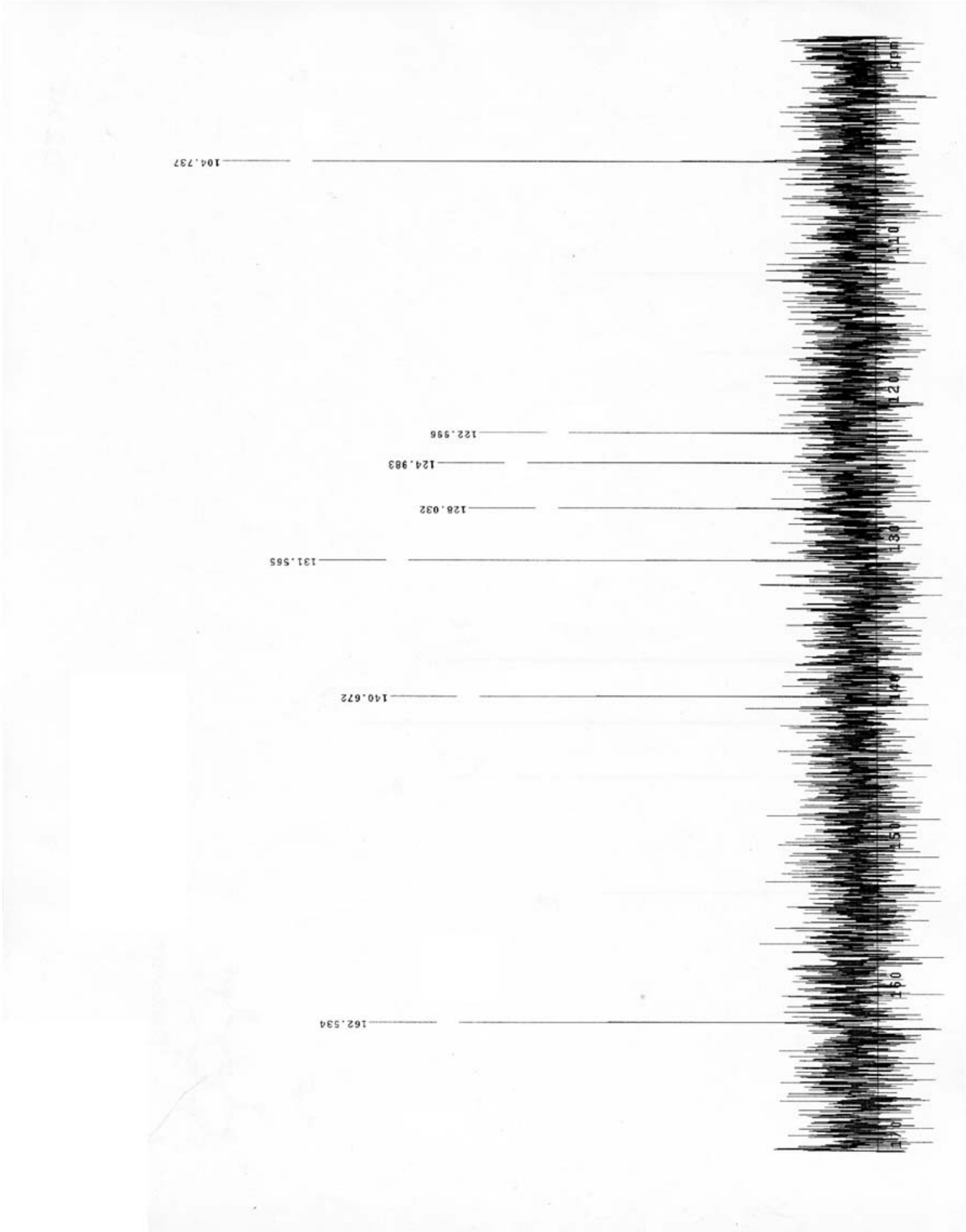
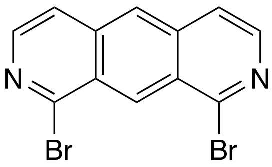


Fig S.6. ^{13}C NMR Spectrum of Compound 6



Compound 7: 1,8-dibromo-2,7-diazaanthracene.



$POBr_3$ (2.42 g, 8.46 mmol), K_2CO_3 (1.17 g, 8.46 mmol) and **6** (300 mg, 1.41 mmol) were refluxed in acetonitrile (60 ml) for 5 hours. The solvent was then evaporated and the solid suspended in ice/water. The pH of the suspension was brought to ≈ 8 using ammonium hydroxide. The water phase was extracted with $CHCl_3$ (3×50 ml). The organic phases were collected and dried over Na_2SO_4 and the solvents evaporated. Column chromatography on SiO_2 ($CHCl_3$) afforded 203 mg (0.6 mmol, 42% yield) of product **7** as a yellow powder. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.47$ (s, 1H), 8.37 (s, 1H), 8.31 (d, $J = 6$ Hz, 2H), 7.76 (d, $J = 6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.8$, 142.0, 136.0, 132.8, 128.2, 126.2, 120.7; ESI-MS m/z calculated for $C_{12}H_7N_2Br_2$ $[M+H]^+$ 339.00, found 339.07.

Fig S.7. ^{1}H NMR Spectrum of Compound 7

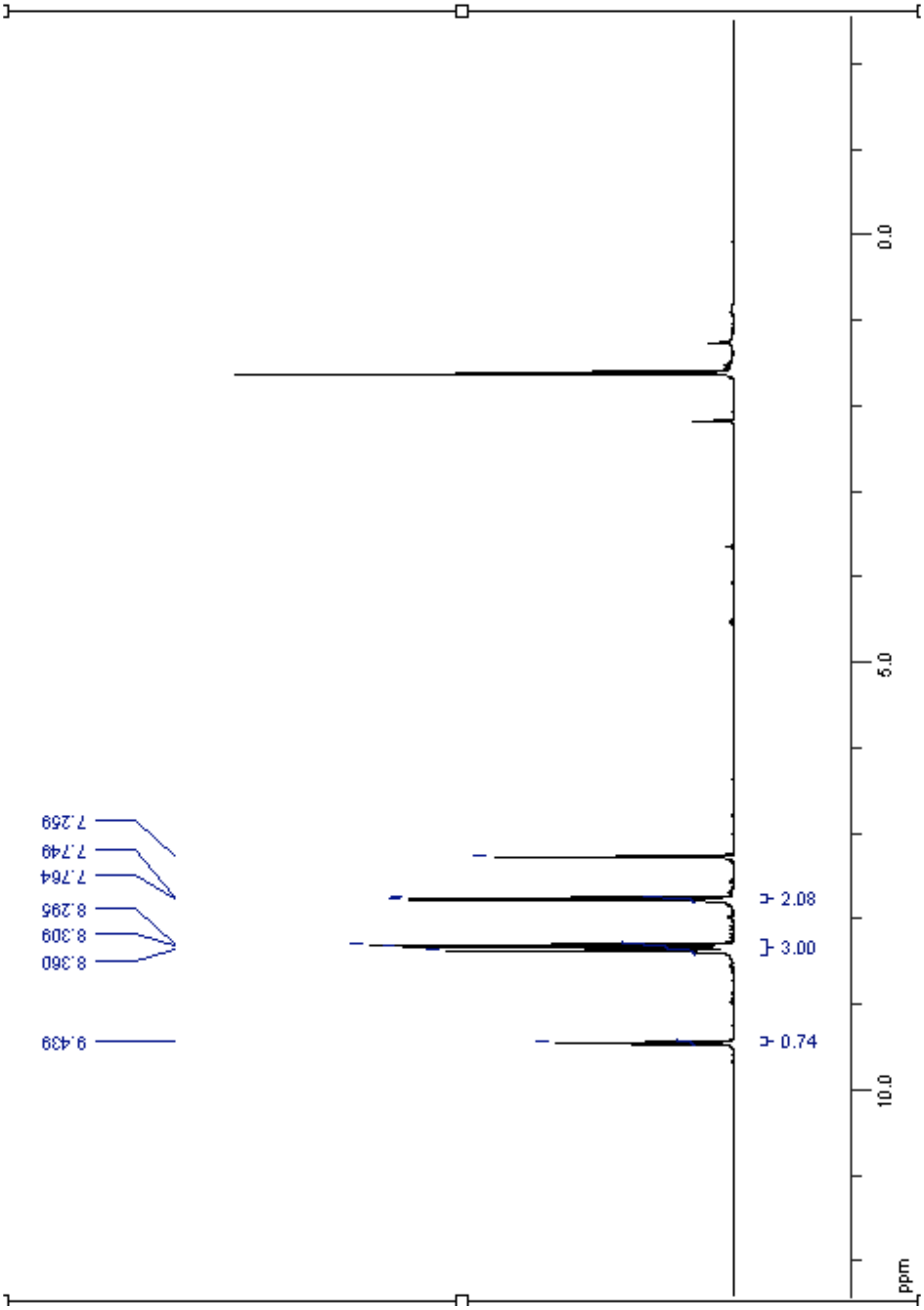
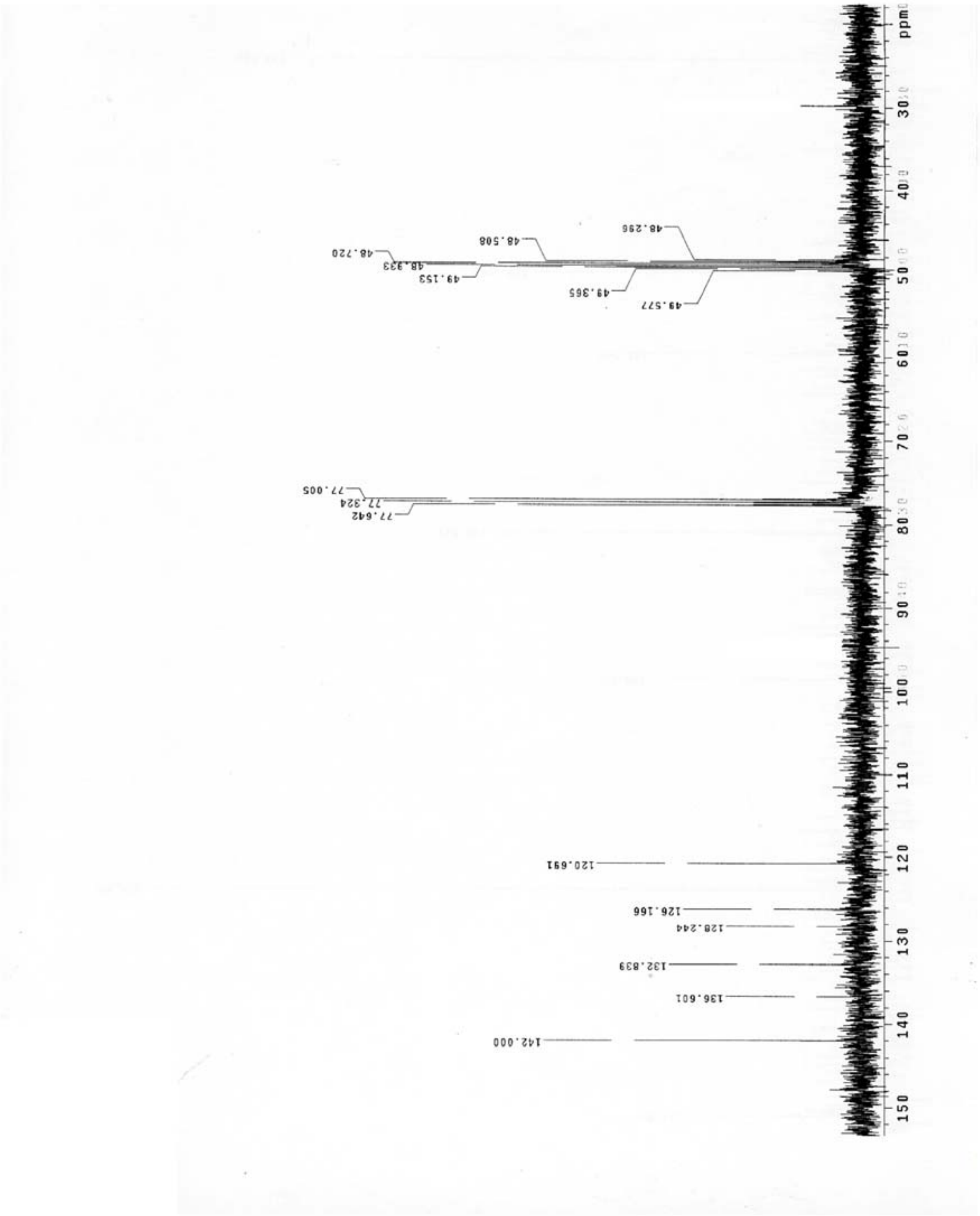
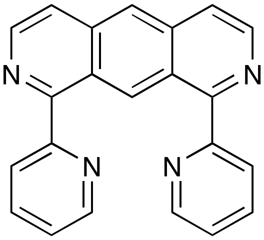


Fig S.8. ^{13}C NMR Spectrum of Compound 7



Compound 1 : 1,8-di(pyridin-2-yl)-2,7-diazaanthracene



Under anhydrous conditions, *n*-BuLi (0.5 ml of a 1.6 M solution in hexanes, 0.72 mmol) was added to a solution of 2-bromopyridine (114 mg, 0.72 mmol) in dry and degassed THF (5 ml) at –78 °C. The solution was stirred for 30 minutes at –78 °C. To this solution was then transferred a solution of $ZnCl_2$ (120 mg, 0.88 mmol) in THF (10 ml) and the reaction mixture was allowed to warm to room temperature. (Note: The zinc chloride was dried under vacuum at 50 °C for 2 days before use). The organozincate was then added to a solution of **7** (80 mg, 0.24 mmol) and $Pd(P(C_6H_5)_3)_4$ (28 mg, 0.024 mmol) in dry THF (5 ml). The reaction mixture was stirred at reflux under argon overnight. Solvents were then evaporated and the solid dissolved in CH_2Cl_2. The organic phase was washed with a saturated solution of EDTA (3×50 ml) and then dried and evaporated. Column chromatography on SiO_2 (MeOH/$CHCl_3$ 3%) afforded 64 mg (0.19 mmol, 80% yield) of product **1** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.44 (s, 1H), 8.74 (d, *J* = 4.8 Hz, 2H), 8.64 (d, *J* = 6 Hz, 2H), 8.45, (s, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 7.93 (dd, *J* = 8 Hz, *J* = 6 Hz, 2H), 7.85 (d, *J* = 6.4 Hz, 2H), 7.43 (dd, *J* = 7.6 Hz, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 157.9, 148.6, 141.7, 137.1, 135.7, 132.0, 125.7, 125.6, 124.1, 123.8, 120.6; ESI-MS *m*/*z* calculated for $C_{22}H_{15}N_4$ [M+H] 335.13, found 335.32. UV (CH_2Cl_2) λ_{max} = 250 nm (ε = 33,300), λ_{max} = 390 nm (ε = 2,750).

Fig S.9. ^{1}H Spectrum of Compound 1

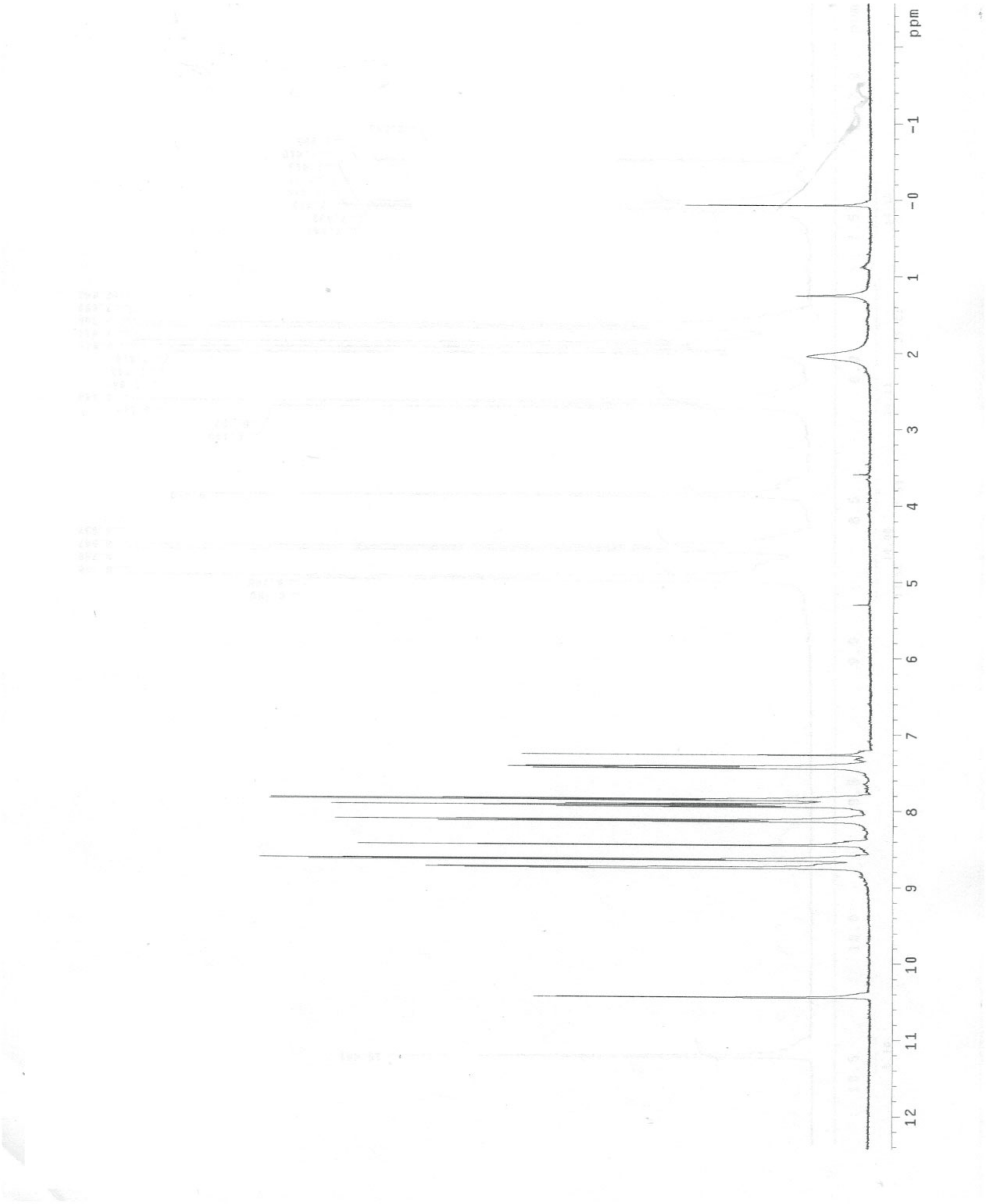
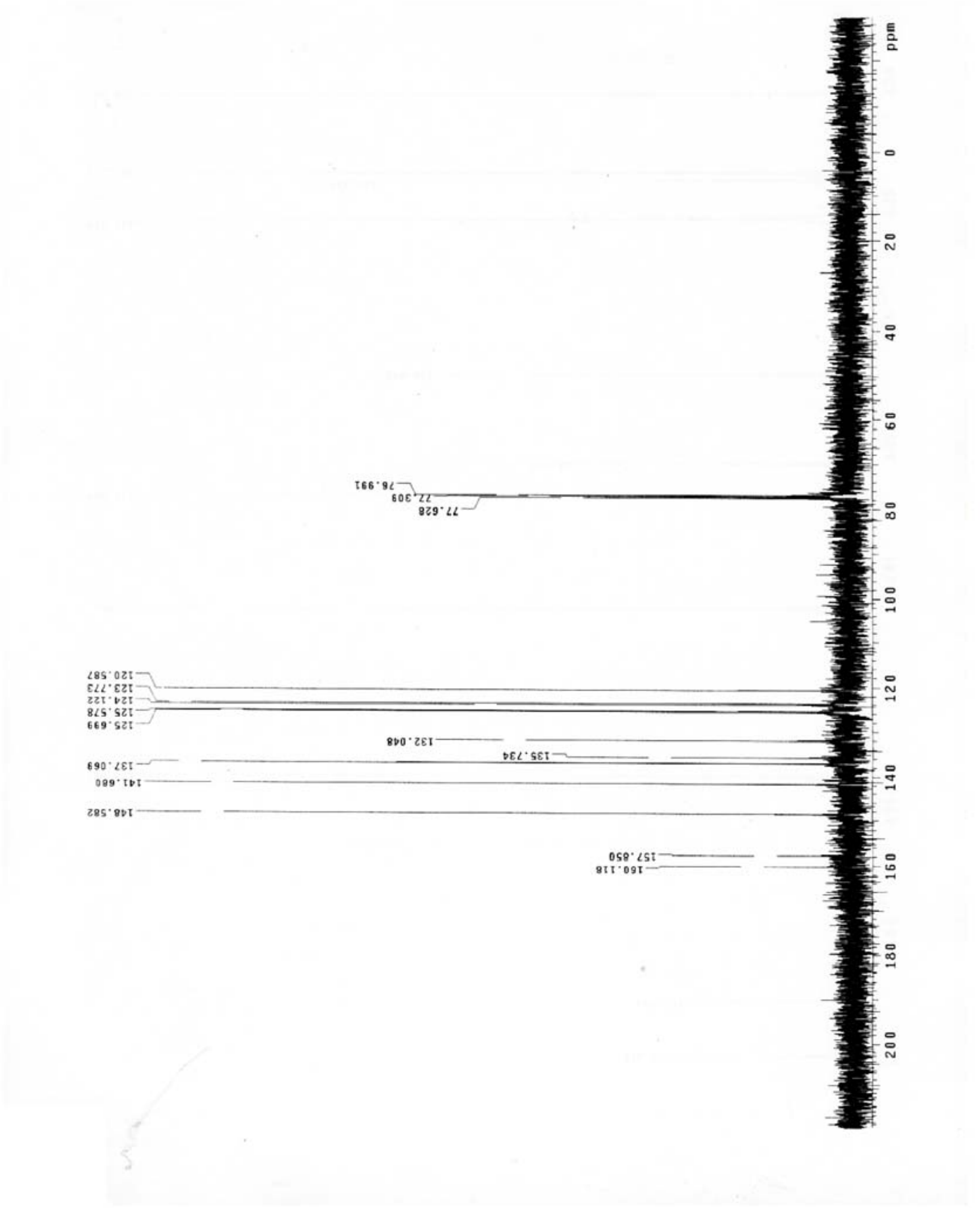
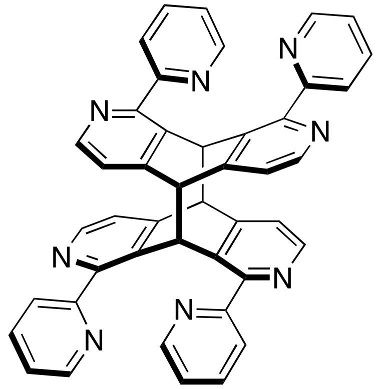


Fig S.10. ^{13}C Spectrum of Compound 1



Compound 2 : 1,8-di(pyridin-2-yl)-2,7-diazaanthracene head-to-tail dimmer



A solution of **1** in degassed acetonitrile was irradiated overnight in a quartz cell at 366 nm. The solvents were then evaporated and the compound was purified by preparative TLC eluting with CHCl3;MeOH 10%, affording **2** as a white powder. . ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.0 Hz, 4H), 8.05 (d, *J* = 4.4 Hz, 4H), 7.79 (dd, *J* = 6.4 Hz, *J* = 7.2 Hz, 4H), 7.70, (d, *J* = 8.4 Hz, 4H), 7.35 (m, 8H), 6.56 (d, *J* = 11.2 Hz, 2H), 5.29 (d, *J* = 10.8 Hz, 2H) ESI-MS *m*/*z* calculated for $C_{44}H_{29}N_8$ [M+H] 669.25, found 669.11. See spectrum in manuscript.

Quantum Yield Determination.

Quantum yields were determined using coumarin 30 as a standard (Du, H.; Fuh, R. A.; Li, J.; Corkan, A.; Lindsey, J. S. *Photochem. and Photobiol.*, **1998**, *68*, 141–142) for ligand **1**. Quantum yields were determined using the following equation:

$\Phi_{F(x)} = (A_s/A_x)\,(F_x/F_s)\,(n_x/n_s)^2\,\Phi_{F(s)}$

where s is the standard, x is the unknown, A is the absorbance at excitation wavelength, F is the area under the emission curve, *n* is the refractive index of the solvent and Φ is the quantum yield (Lavabre, D.; Fery-Forgues, S. *J. Chem. Educ.*, **1999**, *76*, 1260–1264).

The fluorescence quantum yield for compound **1** has been determined to 0.02 in dichloromethane at 25 °C.

Fig S.11. Absorption spectrum of ligand 2 in dichloromethane.

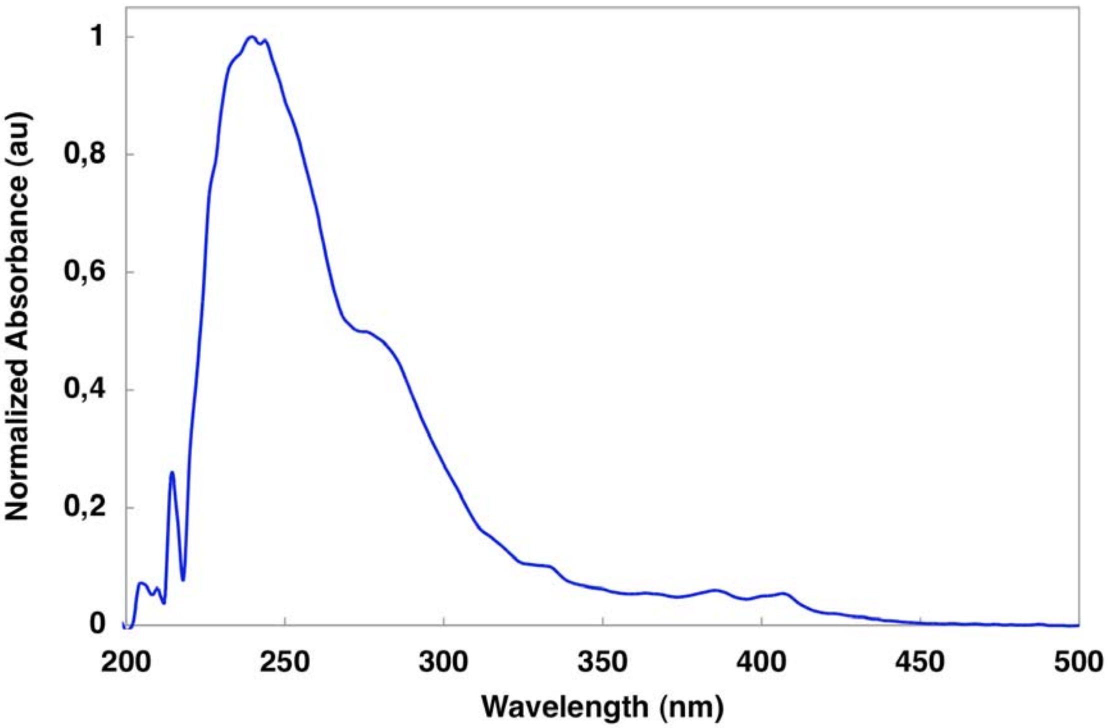
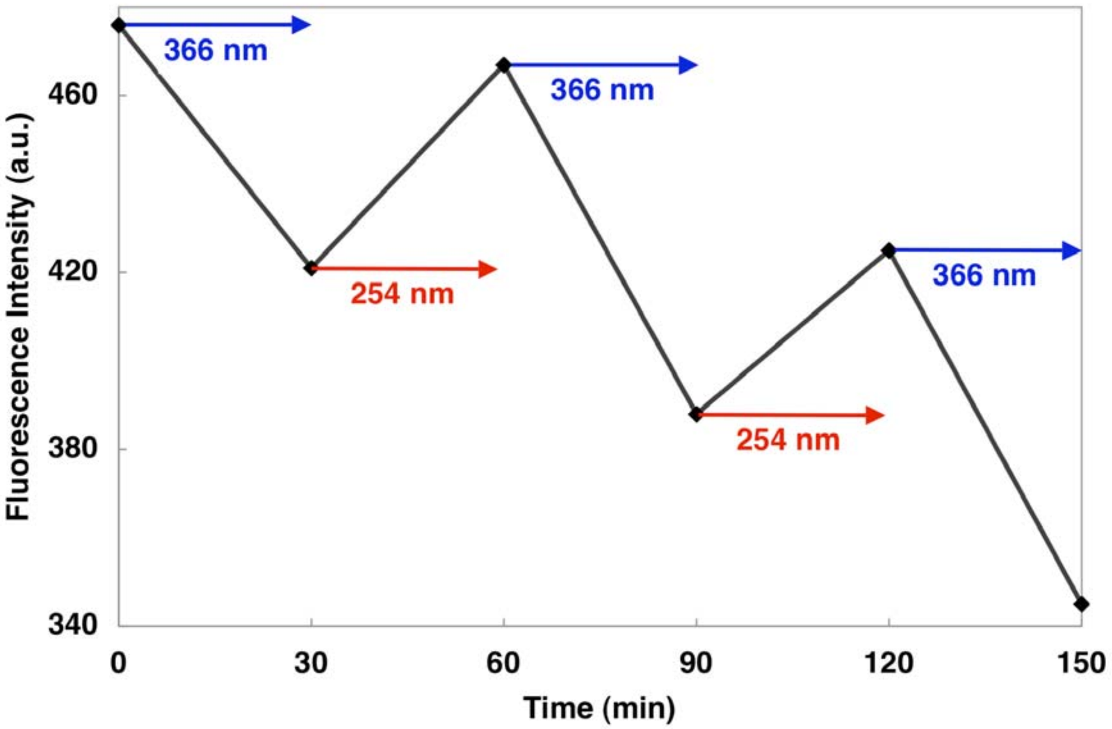
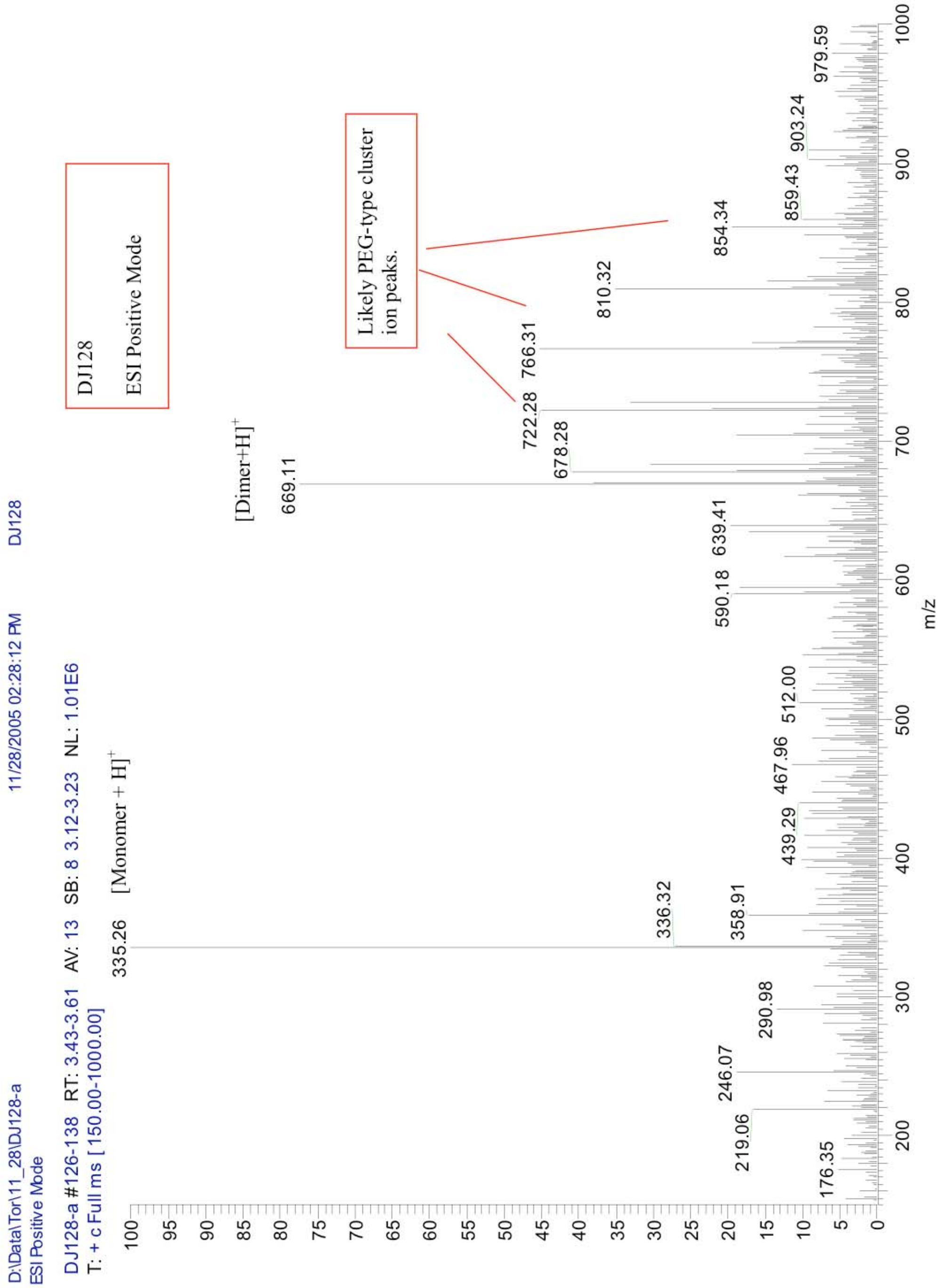


Fig S.12. Fluorescence monitoring of the reversible dimerization.



Compound **1** was irradiated for 30 minutes at 366 nm and then 30 minutes at 254 nm in a degassed solution of acetonitrile for several cycles.

Fig S.13. Mass spectrum of the dimer 2



Crystal data and structure refinement for 1.

Empirical formula	C22 H14 N4	
Formula weight	334.37	
Temperature	218(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 23.964(9) Å	α= 90°.
	b = 6.054(2) Å	β= 90°.
	c = 11.160(4) Å	γ = 90°.
Volume	1619.0(11) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	696	
Crystal size	0.40 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.70 to 28.30°.	
Index ranges	-28<=h<=31, -7<=k<=8, -14<=l<=14	
Reflections collected	11582	
Independent reflections	2019 [R(int) = 0.0434]	
Completeness to theta = 28.30°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9875 and 0.9551	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2019 / 1 / 235	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0940	
R indices (all data)	R1 = 0.0425, wR2 = 0.0966	
Absolute structure parameter	0(10)	
Largest diff. peak and hole	0.211 and -0.201 e.$Å^{-3}$	

Crystal data and structure refinement for 2.

Empirical formula	C44 H28 N8	
Formula weight	668.74	
Temperature	208(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.3433(9) Å	a= 90°.
	b = 12.0224(13) Å	b= 98.373(2)°.
	c = 15.8306(18) Å	g = 90°.
Volume	1571.0(3) Å^3	
Z	2	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	696	
Crystal size	0.40 x 0.35 x 0.30 mm^3	
Theta range for data collection	2.14 to 28.26°.	
Index ranges	-11<=h<=10, -15<=k<=15, -19<=l<=20	
Reflections collected	11563	
Independent reflections	3674 [R(int) = 0.0392]	
Completeness to theta = 28.26°	94.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9745 and 0.9416	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3674 / 0 / 235	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1452	
R indices (all data)	R1 = 0.0766, wR2 = 0.1607	
Largest diff. peak and hole	0.324 and -0.185 e.Å^{-3}	

Fig S.14. UV-Vis spectra of a mono and dinuclear Ru(II) complexes of Ligand 1 in CH_3CN

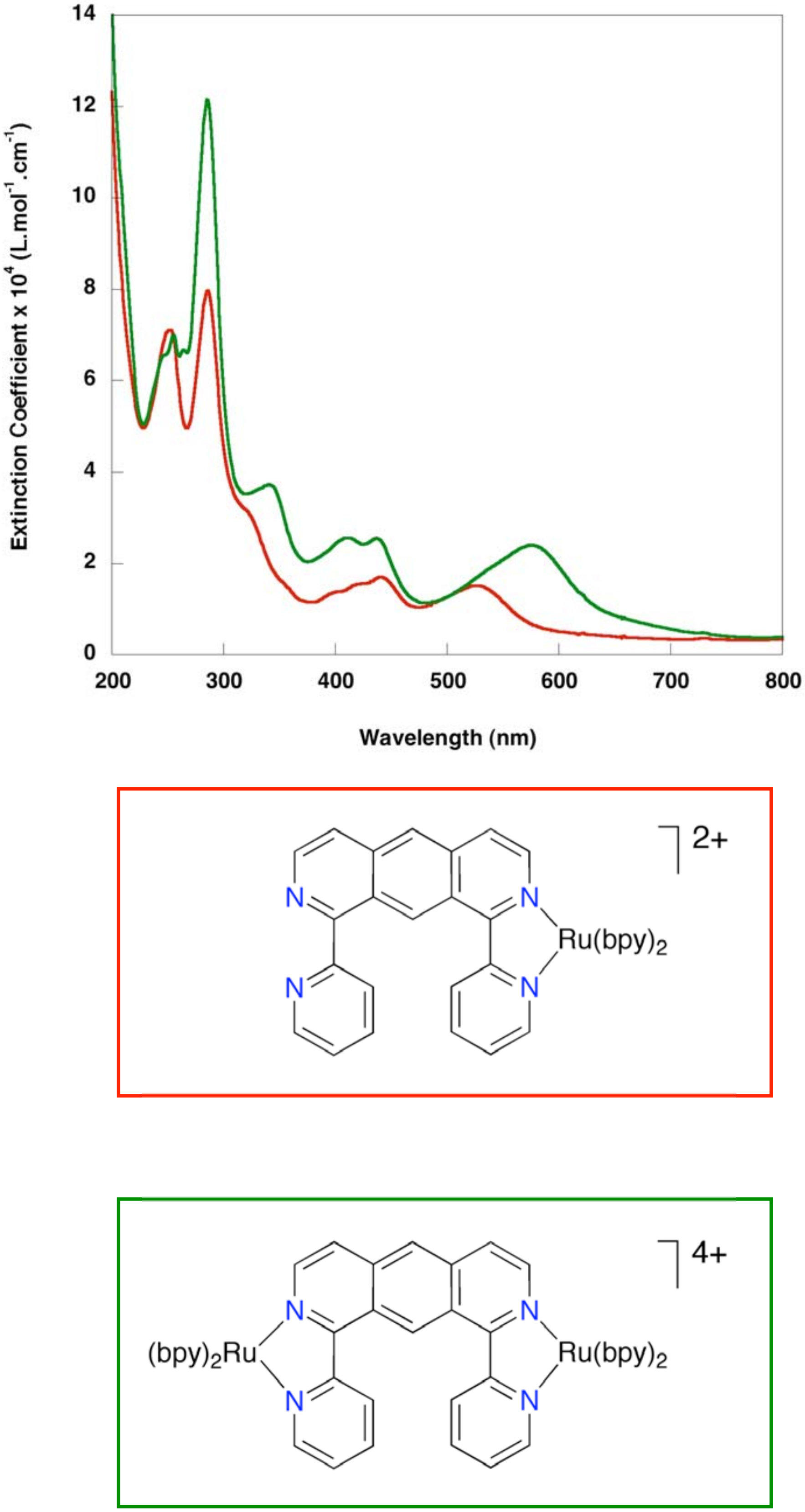
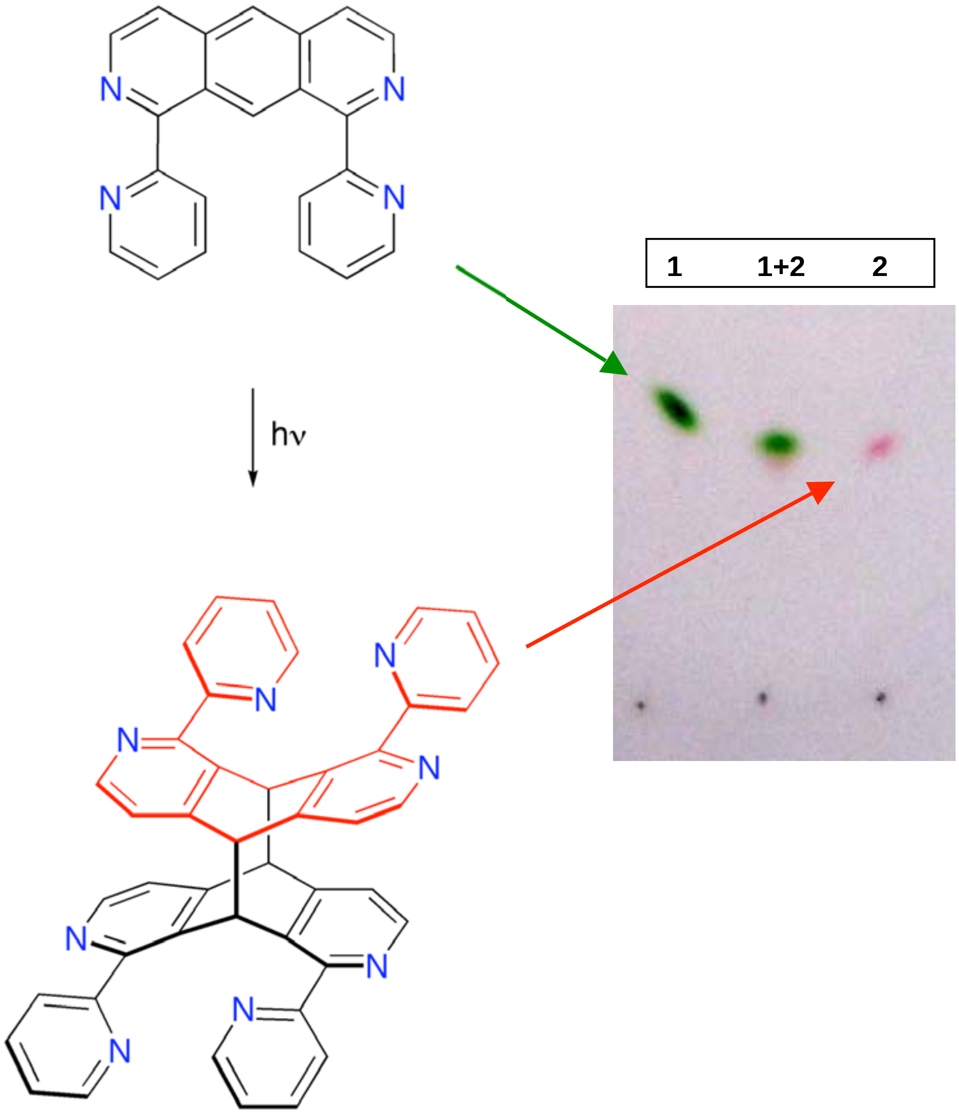


Fig S.15. Reaction of ligands 1 and 2 with Fe^{2+} shows distinct colors



Fe^{2+}-stained TLC plate shows the separation of ligand **1** and **2** and their distinct reaction with a Fe^{2+}, a common visualizing reagent for bpy-type ligands. Note the **red color** displayed by **2**•Fe^{2+} is very similar to the color generated by the parent 2,2'-bipyridine (demonstrating the electronic disconnection between the bpy unit in the photo-dimer), while the **green color** generated by **1**•Fe^{2+}, reflects long-wavelength absorption bands that are a results of the extended conjugation in the precursor monomeric dinuclear ligand **1**.