Supporting Information

A Dinuclear Alkynylplatinum(II) Pyridinedicarboxamide: Conformational Changes Induced Switching of Emission Properties

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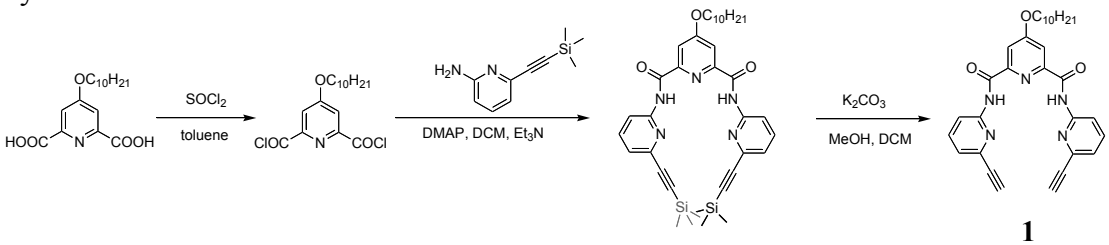
I. Experimental Section.

General Methods. All reagents and dry solvents were purchased from commercial source. Triethylamine was refluxed in the presents of CaH_2 and distilled. Analytical thin-layer chromatography (TLC) was performed on Merck TLC plate (silica gel 60 F254, 0.25 mm). For column chromatography silica gel (Wakogel C-200) was used. The reactions were in general performed under argon atmosphere in anhydrous solvents. NMR spectra were recorded on a JNM-ECS 400 (400 MHz) spectrometer and ^{1}H and ^{13}C chemical shifts are given in ppm and were referenced with the residual solvent resonances relative to tetramethylsilane (TMS). In solvent mixtures TMS was used as an internal standard. Mass spectra were run on a JEOL JMS DX-303 spectrometer. Infrared spectra were obtained with a JASCO FT/IR-4100 spectrometer. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. The X-ray structure measurement were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo K_α radiation. Crystallographic details are given in Table S2 and Table S3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 906709 for compound **1**. Percentages of solvent mixtures are given in volume percent.

Experimental Procedures. 4-Decyloxy-2,6-pyridinedicarboxylic acid was prepared according to the literature method by J.-M. Lehn.[1] Chloro(6-(4-octyloxyphenyl)-2,2'-bipyridine)platinum was prepared according to our previous paper.[2] 2-Amino-6 [(trimethylsilyl)ethynyl]pyridine and 2-amino-6-ethynylpyridine were synthesised according to the literature method by M. Inouye et al.[3]

Synthesis and Characterisation.

Synthesis of **1**:



1

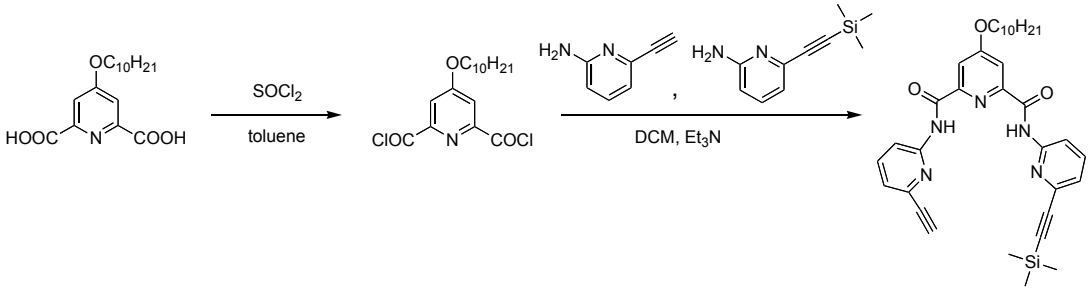
1: Thionyl chloride (6.0 mL, 83 mmol) was added to a solution of 4-decyloxy-2,6-pyridinedicarboxylic acid (650 mg, 2.01 mmol) in toluene 60 mL, which was refluxed at 85 °C for 14 h. After evaporation, the residue was dissolved in dichloromethane. Triethylamine (2.15 mL) and 2-amino-6((trimethylsilyl)ethynyl)pyridine (765 mg, 4.02 mmol) were added and the mixture was stirred for 24 h at room temperature. Then, the organic layer was washed with H_2O and saturated aqueous brine and dried over $MgSO_4$. The residue was purified by column chromatography on silica gel in ethyl acetate/n-hexane (1:1 v/v) to afford a 1:2 mixture of mono- and di-TMS-protected pyridinedicarboxamide derivatives as an off-white solid in a 93% yield calculated for the product mixture (1.20 g, 1.86 mmol).

The product mixture (283 mg, 0.44 mmol) was dissolved in a mixture of anhydrous methanol (40 mL) and dichloromethane (20 mL) and treated with K_2CO_3 (123 mg, 0.89 mmol). The reaction mixture was stirred for 4 h at room temperature. After adding dichloromethane (20 mL), the organic layer was washed with H_2O and saturated aqueous brine and dried over $MgSO_4$. **1** was obtained as an off-white solid in a 98% yield (228 mg, 0.44 mmol).

M.p. 122-124 ºC; IR (KBr): 3367 (m; ν($CONH_{weak}$)), 3289 (m; ν(C≡C-H)), 3263 (m; ν($CONH_{strong}$)), 2925 (m; ν(CH_2)), 2854 (m; ν(C-H)), 1697 (s; ν(C=O)), 1587, 1573 (s; ν(C=N)) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.51 (s, 2H), 8.48 (dd, 2H, J = 8.4, 0.8 Hz), 7.97 (s, 2H), 7.83–7.76 (m, 2H), 7.33 (dd, 2H, J = 7.6, 0.8 Hz), 4.22 (t, 2H, J = 6.8 Hz), 3.24 (s, 2H), 1.87 (quint, 2H, J = 6.8 Hz), 1.54–1.45 (m, 2H), 1.43–1.22 (m, 12H), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) 168.8, 162.2, 151.6, 150.8, 140.7, 139.2, 124.2, 114.8, 112.5, 82.5, 77.4, 69.8, 32.3, 29.9, 29.7, 29.6, 29.1, 26.2, 23.1, 14.2 ppm; HRMS (FAB) calculated for $C_{31}H_{34}N_5O_3$ ([M+H]$^+$)

524.2656, found *m/z* 524.2656. Anal. Calcd. for $C_{31}H_{33}N_5O_3 \cdot CH_3OH$: C, 69.17; H, 6.71; N, 12.60, found C, 69.31; H, 6.56; N, 12.45.

Synthesis of **2**:



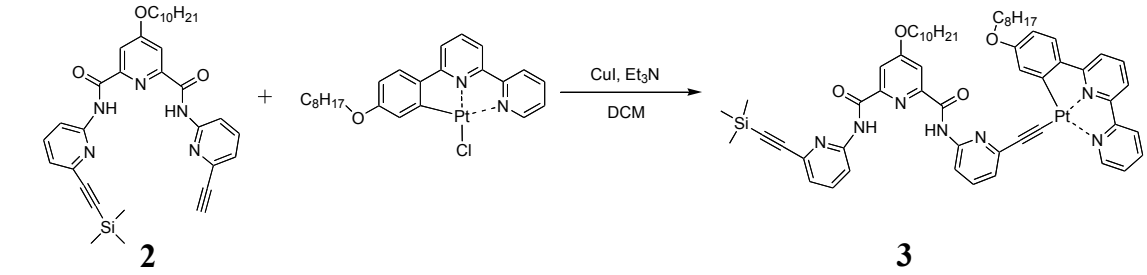
2

2: Thionyl chloride (6.0 mL, 83 mmol) was added to a solution of 4-decyloxy-2,6-pyridinedicarboxylic acid (800 mg, 2.47 mmol) in toluene (60 mL) and was refluxed at 85 °C for 14 h. After evaporation, the residue was dissolved in dichloromethane (25 mL). Triethylamine (2.15 mL), a catalytic amount of 4-dimethylaminopyridine, 2-amino-6-ethynylpyridine (295 mg, 2.50 mmol) and 2-amino-6 [(trimethylsilyl)ethynyl]pyridine (476 mg, 2.50 mmol) were added and the mixture was stirred for 24 h at room temperature, then the organic layer was washed with H_2O and saturated aqueous brine and dried over $MgSO_4$. The residue was purified by column chromatography on silica gel in ethyl acetate/n-hexane (9:1 v/v) to afford the isolated compound **2** as an off-white solid in a 32% yield (476 mg, 0.80 mmol). Furthermore, the di-TMS protected derivative (25%, 408 mg, 0.61 mmol) and **1** (17%, 216 mg, 0.41 mmol) could be obtained.

M.p. 139–141 ºC; IR (KBr): 3366 (w; ν($CONH_{weak}$)), 3310 (w; ν(C≡C-H)), 3257 (m; ν($CONH_{strong}$)), 2925 (s; ν(CH_2)), 2854 (m; ν(C-H)), 1693 (s; ν(C=O)), 1586, 1574 (s; ν(C=N)) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 10.49 (s, 1H), 10.48 (s, 1H), 8.52 (dd, 1H, J = 8.4, 0.8 Hz), 8.47 (dd, 1H, J = 8.4, 0.8 Hz), 7.98 (s, 2H), 7.79 (dd, 2H, J = 8.4, 7.5 Hz), 7.34 (dd, 1H, J = 7.5, 0.8 Hz), 7.30 (dd, 1H, J = 7.5, 0.8 Hz), 4.22 (t, 2H, J = 6.8 Hz), 3.18 (s, 1H), 1.87 (quint, 2H, J = 6.8 Hz), 1.54–1.45 (m, 2H), 1.43–1.24 (m, 12H), 0.89 (t, 3H, J = 6.8 Hz), 0.28 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) 168.7, 162.2, 162.1, 151.7, 151.6, 150.9, 141.4, 140.7, 139.2, 139.1, 124.3, 124.0, 114.9, 114.4, 112.5, 103.5, 95.2, 82.6, 77.4, 69.8, 32.3, 30.1, 29.9, 29.7, 29.6, 29.1, 26.2, 23.1, 14.3, -0.2 ppm. HRMS (FAB) calculated for $C_{34}H_{41}N_5O_3Si$ ($[M+H]^+$)

596.3051, found *m/z* 596.3060. Anal. Calcd. for $C_{34}H_{41}N_5O_3Si$: C, 68.54; H, 6.94; N, 11.75, found C, 68.28; H, 6.76; N, 11.73.

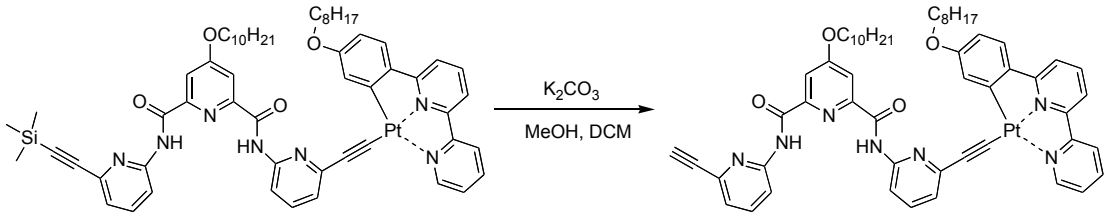
Synthesis of the platinum(II) complex **3**:



2 **3**

3: Chloro(6-(4-octyloxyphenyl-2,2'-bipyridine)platinum (158 mg, 0.27 mmol), **2** (200 mg, 0.34 mmol) and CuI (6 mg, 0.03 mmol) were dissolved in dichloromethane (10 mL) and triethylamine (1.1 mL) was added. The reaction mixture was stirred for 20 h at room temperature in the absence of light. Then, H_2O was added and the organic layer was washed with H_2O and saturated aqueous brine and dried over $MgSO_4$. The solvent was then evaporated to dryness under reduced pressure and the crude product was purified by column chromatography on silica gel in dichloromethane/ethyl acetate (97:3 v/v) to afford **3** as an orange-red solid in a 42% yield (130 mg, 0.11 mmol).

Synthesis of the platinum(II) complex **MonoPt**:

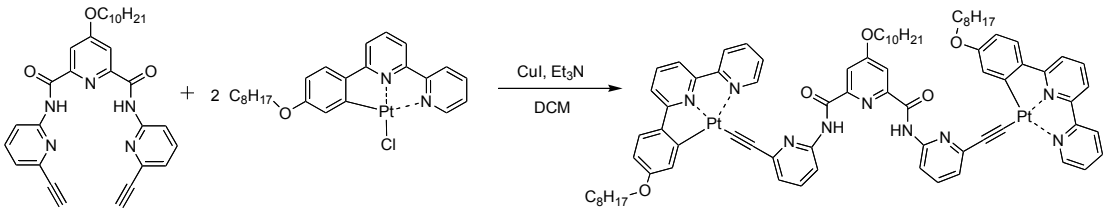


3 **MonoPt**

MonoPt: K_2CO_3 (12 mg, 0.087 mmol) and **3** (100 mg, 0.087 mmol) were dissolved in a mixture of anhydrous methanol (20 mL) and dichloromethane (20 mL). The reaction mixture was stirred for 4 h at room temperature and was washed with H_2O and saturated aqueous brine and dried over $MgSO_4$. **MonoPt** was obtained as a dark red solid in a 97% yield (91 mg, 0.084 mmol).

M.p. 195–197 ºC; IR (KBr): 3373 (w; ν(CONH$_{weak}$)), 3266 (br; ν(CONH$_{strong}$)), 2924 (s; ν(CH$_2$)), 2853 (m; ν(C-H)), 1696 (s; ν(C=O)), 1586 (s; ν(C=N)) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.89 (s, 1H), 10.78 (s, 1H), 9.23 (dd, 1H, J = 5.4, 0.9 Hz), 8.46 (dd, 1H, J = 8.4, 0.8 Hz), 8.27 (dd, 1H, J = 8.2, 0.8 Hz), 8.07–8.01 (m, 1H), 8.00–7.93 (m, 2H), 7.93 (d, 1H, J = 8.0 Hz), 7.85–7.78 (m, 1H), 7.77–7.68 (m, 2H), 7.60–7.52 (m, 2H), 7.50 (d, 1H, J = 8.2 Hz), 7.45 (dd, 1H, J_{Pt-H} = 35.5, J = 2.4 Hz), 7.36 (d, 1H, J = 8.8 Hz), 7.27 (dd, 1H, J = 7.6, 0.8 Hz), 7.18 (dd, 1H, J = 7.5, 0.8 Hz), 6.59 (dd, 1H, J = 8.5, 2.8 Hz), 4.23 (t, 2H, J = 6.8 Hz), 4.04 (t, 2H, J = 6.8 Hz), 2.70 (s, 1H), 1.87 (quint, 2H, J = 6.8 Hz), 1.70 (quint, 2H, J = 6.8 Hz), 1.55–1.46 (m, 2H), 1.43–1.15 (m, 22H), 0.89 (t, 3H, J = 6.8 Hz), 0.83 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) 168.7, 165.4, 162.5, 162.1, 161.9, 158.4, 154.7, 152.2, 151.9, 151.2, 151.1, 150.7, 146.0, 144.9, 140.6, 139.4, 139.3, 139.1, 138.5, 128.2, 126.5, 123.7, 123.6, 123.4, 123.1, 118.2, 117.0, 114.8, 112.2, 112.1, 110.9, 110.5, 105.4, 82.3, 77.8, 69.8, 68.3, 32.3, 32.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.2, 26.4, 26.2, 23.1, 23.0, 14.3, 14.2 ppm. HRMS (FAB) calculated for $C_{55}H_{59}N_7O_4Pt$ ([M+H]$^+$) 1077.4349, found m/z 1077.4341. Anal. Calcd. for $C_{55}H_{59}N_7O_4Pt\cdot 2H_2O$: C, 59.34; H, 5.70; N, 8.81. Found: C 59.26; H, 5.66; N, 8.74.

Synthesis of the platinum(II) complex **DiPt**:



1 **DiPt**

DiPt: Chloro(6-(4-octyloxy-phenyl-2,2'-bipyridine)platinum (113 mg, 0.19 mmol), **1** (50 mg, 0.096 mmol), CuI (3.6 mg, 0.019 mmol) were dissolved in 5 mL dichloromethane. After addition of triethylamine (650 μL) the mixture was stirred for 20 h in the dark at room temperature and was washed with saturated aqueous $NaHCO_3$, H_2O and saturated aqueous brine, dried over $MgSO_4$ and filtrated. The filtrate was concentrated by evaporation. The residue was purified by preparative thin-layer chromatography using dichloromethane/methanol (97:3 v/v) as mobile phase to afford **DiPt** as an orange solid (24% yield, 37 mg, 0.023 mmol).

M.p. 215–217 ºC; IR (KBr): 3263 (br; ν($CONH_{strong}$)), 2923 (s; ν(CH_2)), 2852 (m; ν(C-H)), 1686 (s; ν(C=O)), 1587 (s; ν(C=N)) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 11.60 (s, 2H), 9.39 (dd, 2H, J = 5.2, 0.8 Hz), 8.30 (dd, 2H, J = 8.0, 0.8 Hz), 7.99 (s, 2H), 7.74 (td, 2H, J = 7.8, 1.6 Hz), 7.71 (t, 2H, J = 8.0 Hz), 7.42 (d, 2H, J = 8.0 Hz), 7.39–7.33 (m, 4H), 7.07–6.99 (m, 6H), 6.97 (dd, 2H, J_{Pt-H} = 35.3, J = 2.8 Hz), 6.81 (d, 2H, J = 7.8 Hz), 6.55 (dd, 2H, J = 8.4, 2.8 Hz), 4.18 (t, 2H, J = 6.8 Hz), 4.08 (t, 4H, J = 6.8 Hz), 1.93–1.86 (m, 6H), 1.63–1.52 (m, 6H), 1.50–1.20 (m, 28H), 0.92 (t, 6H, J = 6.8 Hz), 0.90 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) 168.9, 164.1, 162.3, 161.2, 158.1, 155.5, 153.0, 151.5, 151.0, 139.8, 138.9, 138.5, 138.1, 131.3, 129.1, 128.6, 126.1, 122.7, 122.4, 116.9, 116.2, 113.2, 111.8, 110.4, 109.7, 104.6, 69.8, 68.2, 32.3, 30.1, 29.9, 29.8, 28.7, 26.6, 26.2, 23.1, 14.3 ppm. HRMS (FAB) calculated for $C_{79}H_{86}N_9O_5Pt_2$ ($[M+H]^+$) 1630.6042, found m/z 1630.6102. Anal. Calcd.: C, 58.19; H, 5.25; N, 7.73, found C, 58.20; H, 5.35; N, 7.45.

Physical Measurements.

UV-vis spectra were obtained using a Hitachi U-3500 spectrophotometer equipped with a temperature controller SDR-30 in deaerated solvent under argon. Quartz cuvettes with 10 mm path length were used for this purpose. Emission spectra were collected using a Shimadzu RF-5300PC spectrofluorophotometer in deaerated solvent under argon, using 5 mm or 10 mm path length quartz cuvettes and a filter set. Lifetime measurements were performed on a Hamamatsu, compact fluorescence lifetime spectrometer, Quantaurus-Tau C11367. Concentrations for UV-vis and emission studies were 2.5 x 10^{-5} M of the mononuclear and dinuclear compounds, whereas for ^1H NMR measurements the concentration of 1 x 10^{-3} M was used. All measurements were performed at 298 K unless otherwise stated.

^1H NMR titration:

The $CDCl_3$ solution of **DiPt** (1.0×10^{-3} M) containing various concentrations of methanol (0%–50%) was prepared and ^1H NMR spectra were measured, after 1 h incubation, at 295 K. The changes in the chemical shift of signals of **DiPt** as a function of the methanol concentration were then analyzed. The chemical shifts were plotted against the methanol concentration.

Emission titration:

The dichloromethane solution of **DiPt** (2.5×10^{-5} M) containing various concentrations of methanol (0%–50%) was prepared and emission spectra were measured at 298 K. Sample preparation was carried out by drying the sample carefully at reduced pressure and afterwards dissolving the sample in the solvent mixture and kept at 298 K for 1 h before usage.

Low temperature emission measurement:

The variable temperature emission was measured on an Oxford Instruments Optistat DN liquid-nitrogen-cooled cryostat system complete with an Oxford Instruments temperature controller using a 10 mm path length quartz cuvettes. The used excitation wavelength was 370 nm, with the scattered light removed by a filter set. The sample was cooled to 193 K and warmed up to 293 K emission spectra were measured at several intermediate temperatures (20 K steps) after at least 30 min in which the sample was allowed to equilibrate.

High temperature UV-vis and Emission measurement:

Samples of **DiPt** (2.5×10^{-5} M) were prepared (first, drying the sample under reduced pressure and afterwards dissolving **DiPt** in 1,2-dichloroethane or 10% methanol in 1,2-dichloroethane). The samples were kept at 298 K for 1 h before usage. Emission and UV-vis spectra were measured at 298 K, then UV-vis samples were heated up to 303 K, 313 K, 318 K and 323 K and were measured at each intermediate temperature after 30 min in which the sample was allowed to equilibrate. The temperature was kept for 1 h at 323 K, afterwards they were cooled down to 298 K and kept at 298 K till no changes were detectable. From these samples the emission spectra were measured.

II. Spectra and Figures: Synthesis and Characterisation

Table S1. Selected spectroscopic data for **1-3, MonoPt** and **DiPt**.

Compound	^{1}H NMR N-H (ppm) [a] CD_2Cl_2	FT-IR ν_{N-H} (cm^{-1}) KBr	FT-IR ν_{N-H} (cm^{-1}) [b] CH_2Cl_2
1	10.51	3367 (s)	3367 (s)
		3263 (m)	-
2	10.49	3366 (w)	3367 (s)
	10.48	3257 (s)	-
3	10.45	3378 (w)	3366 (s)
	10.39	3275 (s)	3297 (w)
MonoPt	10.89	3373 (w)	3364 (s)
	10.78	3266 (s)	3280 (w)
DiPt	11.60	-	3363 (w)
		3263 (s)	3282 (s)

[a] 1.0 x 10^{-3} M; [b] 5.0 x 10^{-3} M. s: strong; m: medium strong; w: weak.

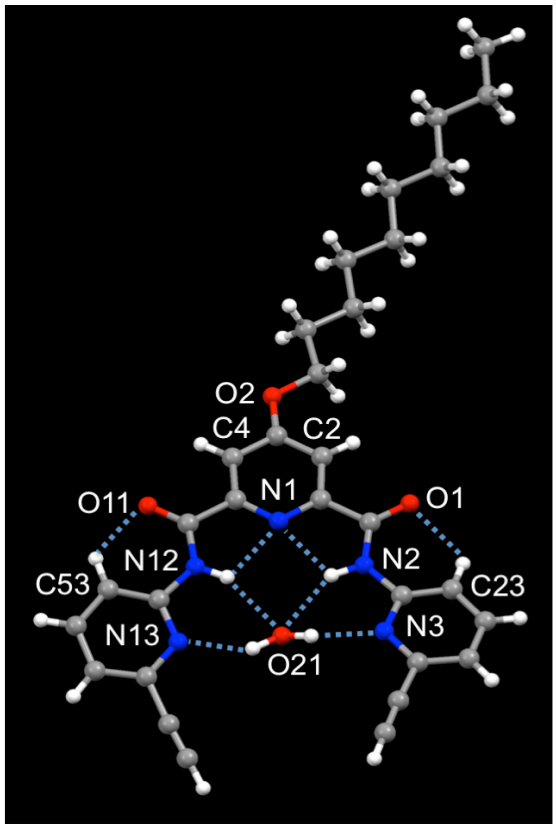


Fig. S1: Crystal structure of **1**. Crystals grown from dichloromethane-n-hexane.

Table S2. Crystallographic data for **1**.

formula	$C_{31}H_{33}N_5O_3 \cdot H_2O$
formula weight	541.64
crystal system	monoclinic
space group	*Cc* (No. 9)
a, Å	20.1413(4)
b, Å	10.5332(2)
c, Å	13.5163(3)
β, deg	95.836(1)
V, Å^3	2852.7(9)
Z	4
D_{calcd}, g cm^{-3}	1.261
μ(Cu-Kα), cm^{-1}	6.868
T, °C	-150.0
λ(Cu-Kα), Å	1.54187
*R*1 [a]	0.0462
*wR*2 [b]	0.2013

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S3. Hydrogen bonds for **1**.

type [a]	donor	acceptor	D • • • A (Å)	D–H • • • A (°)
inter	O(21)	N(3)	2.875(5)	157(4)
inter	O(21)	N(13)	2.817(5)	143(5)
inter	N(2)	O(21)	2.994(4)	146(18)
intra	N(2)	N(1)	2.663(5)	111.4(14)
inter	N(12)	O(21)	3.037(5)	149.2(14)
intra	N(12)	N(1)	2.660(4)	111.5(13)
intra	C(23)	O(1)	2.879(5)	120.5
intra	C(53)	O(11)	2.867(5)	118.8

[a] inter: intermolecular, intra: intramolecular.

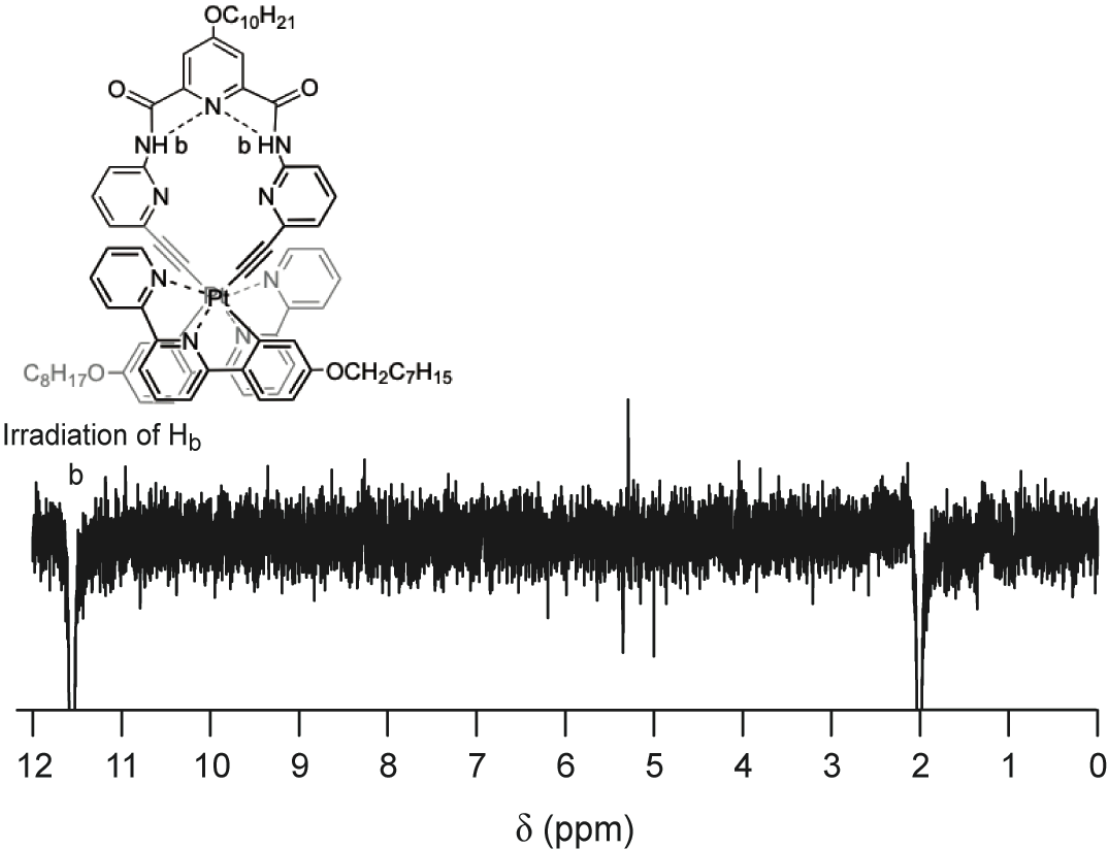


Fig. S2: 400 MHz ^{1}H NMR difference NOE experiment performed at 298 K, 1.0 x 10^{-3} M solution of **DiPt** in CD_2Cl_2.

No NOE interaction of H_b with other protones was observed. Supporting complex **DiPt** is present in a closed conformation A. In contrary, if **DiPt** would adopt the open form B, an interaction of H_b and H_e should be detectable as implied in Fig. S2a.

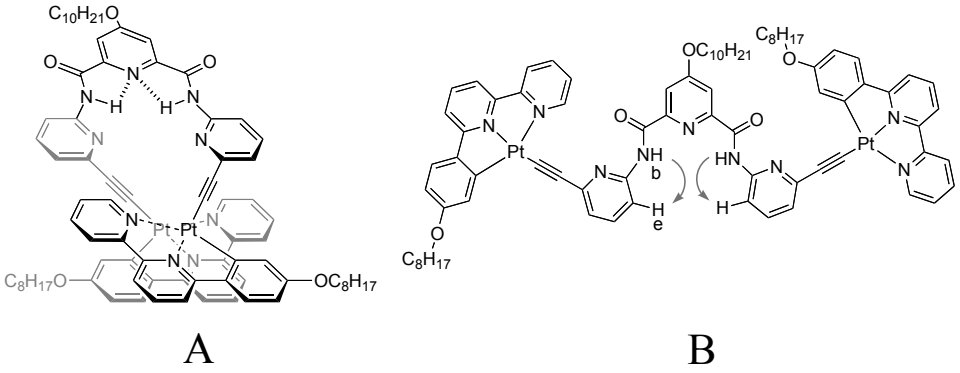


Fig. S2a: Closed (A) and open (B) form of complex **DiPt**.

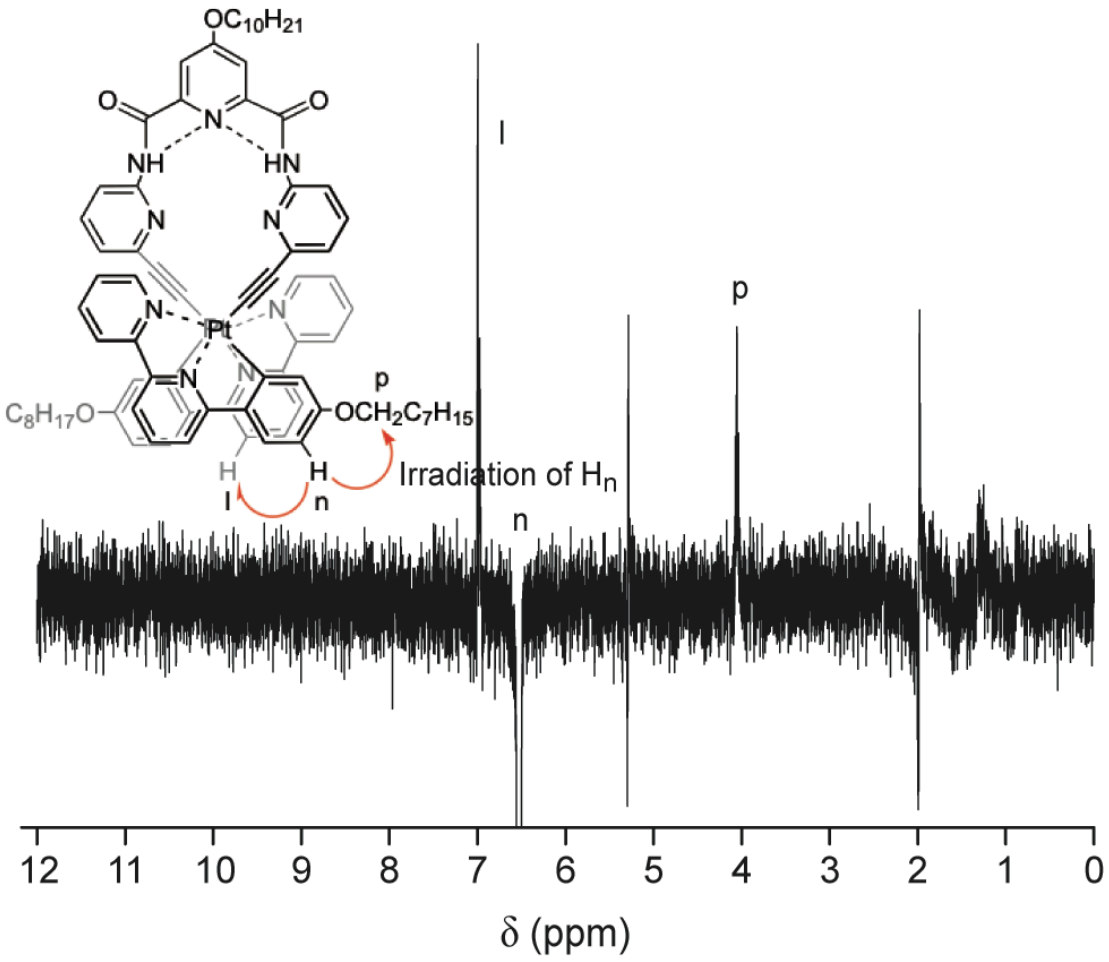


Fig. S3: 400 MHz ^{1}H NMR difference NOE experiment performed at 298 K, 1.0 x 10^{-3} M solution of **DiPt** in CD_2Cl_2.

Irradiation of H_n shows an NOE interaction to H_p and H_l. Interaction to H_l of the facing side supports the presence of conformation A_1 (Fig. S3a).

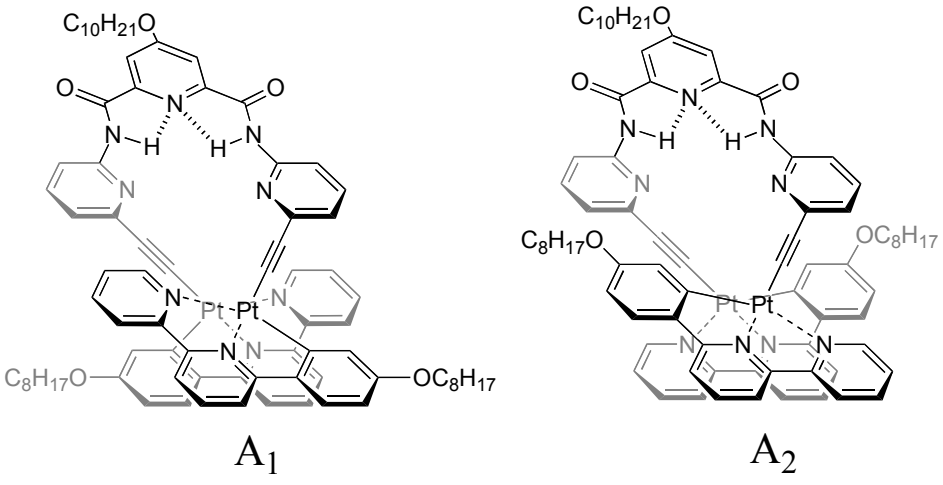


Fig. S3a: Possible closed conformations of complex **DiPt**.

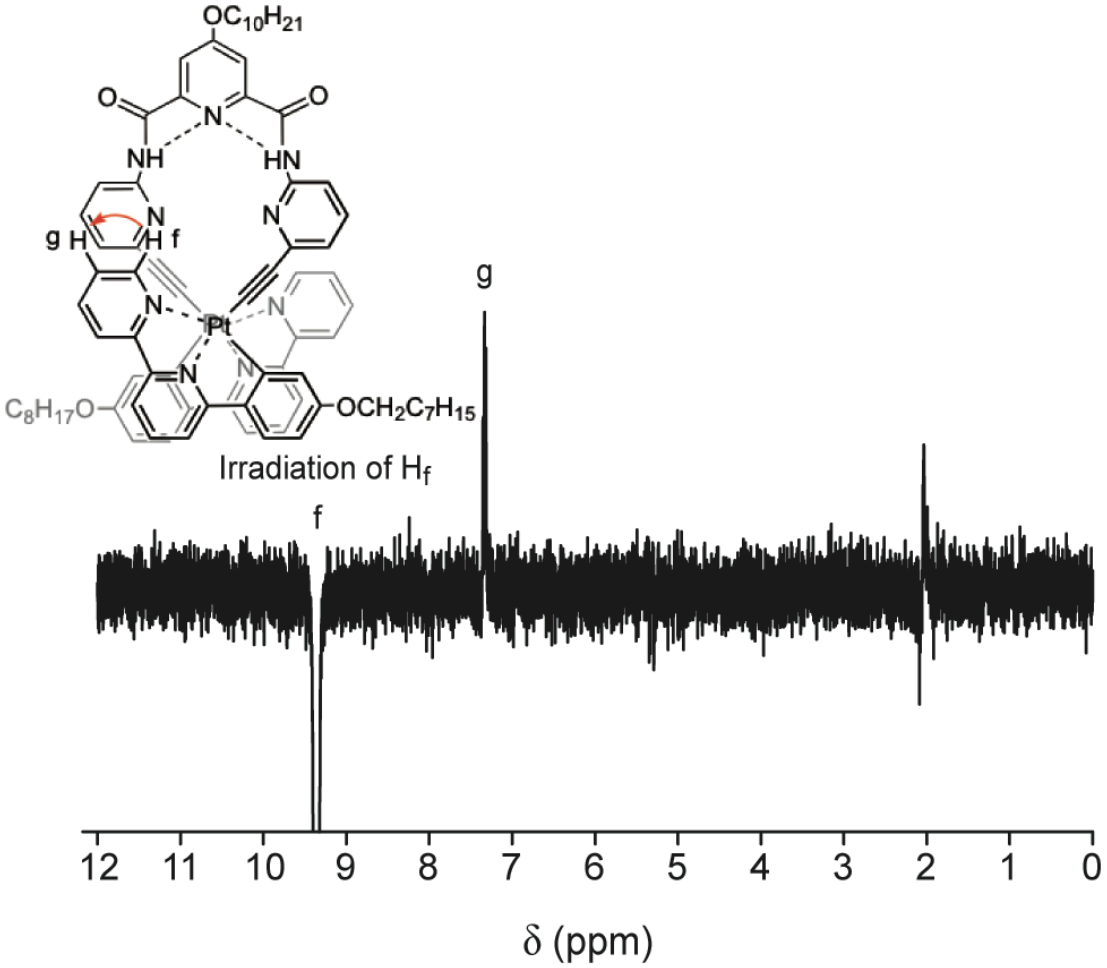


Fig. S4: 400 MHz ^{1}H NMR difference NOE experiment performed at 298 K, 1.0 x 10^{-3} M solution of **DiPt** in CD_2Cl_2.

Irradiation of H_f shows only an NOE interaction with its neighbour proton H_g, which supports conformation A_1 (Fig. S3a).

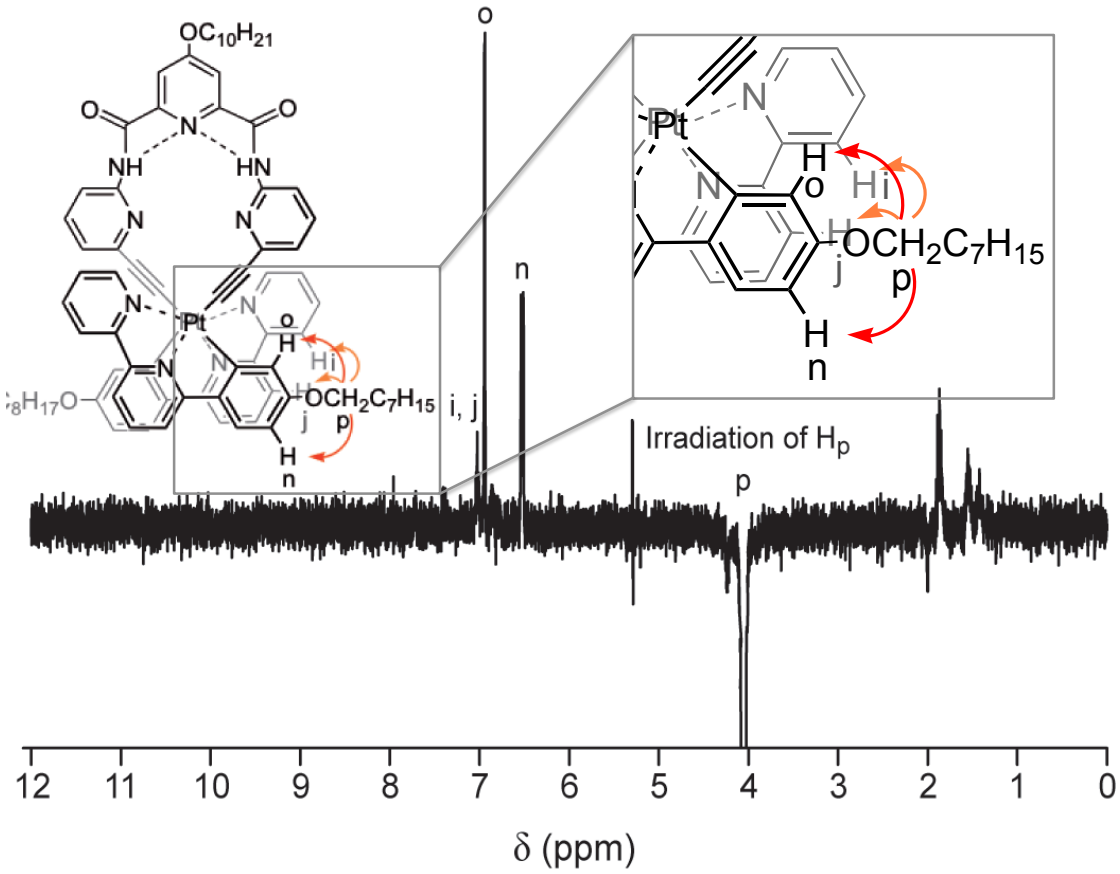


Fig. S5: 400 MHz ^{1}H NMR difference NOE experiment performed at 298 K, 1.0 x 10^{-3} M solution of **DiPt** in CD_2Cl_2.

Irradiation of H_p reveals an interaction to the close protons H_n and H_o, but also to the facing side's protons H_i and H_j, which supports conformation A_1 (Fig. S3a).

III. Spectra and Figures: Methanol Addition

Table S4. Emission lifetimes for **MonoPt** and **DiPt**.

Complex	Solvent	λ_{em}[a] (nm)	n[b]	τ_1 (ns)[c]	A_1	τ_2 (ns)[c]	A_2	τ_3 (ns)[c]	A_3	χ^2
MonoPt	CH_2Cl_2	600	1	268						1.0
DiPt	CH_2Cl_2	600	2	13	0.34	307	0.66			1.1
		750	2	47	0.82	101	0.18			1.1
	MeOH/CH_2Cl_2	600	2	6	0.14	319	0.86			1.0
	(1:1)	750	3	35	0.82	96	0.07	319	0.11	1.1

[a] λ_{ex} = 365 nm. [b] Number of components. [c] Measured at a concentration of 2.5 x 10^{-5} M for **MonoPt** and 1.25 x 10^{-5} M for **DiPt** at room temperature under air by the time-correlated single-photon-counting technique (error ± 0.1 ns) monitoring λ_{em}.

Table S5. Quantum yields for **MonoPt** and **DiPt**.

Complex	Solvent	Φ_{lum} x 10^2 [a]
MonoPt	CH_2Cl_2	2.57
DiPt	CH_2Cl_2	0.42
	MeOH/CH_2Cl_2 (1:1)	1.27

[a] λ_{ex} = 350 nm. Measurment was performed at room temperature in deaerated solvent. The solvent was degassed by at least three successive freeze-pump-thaw cycles. Quinine sulfate in 1 N H_2SO_4 was used as the standard.

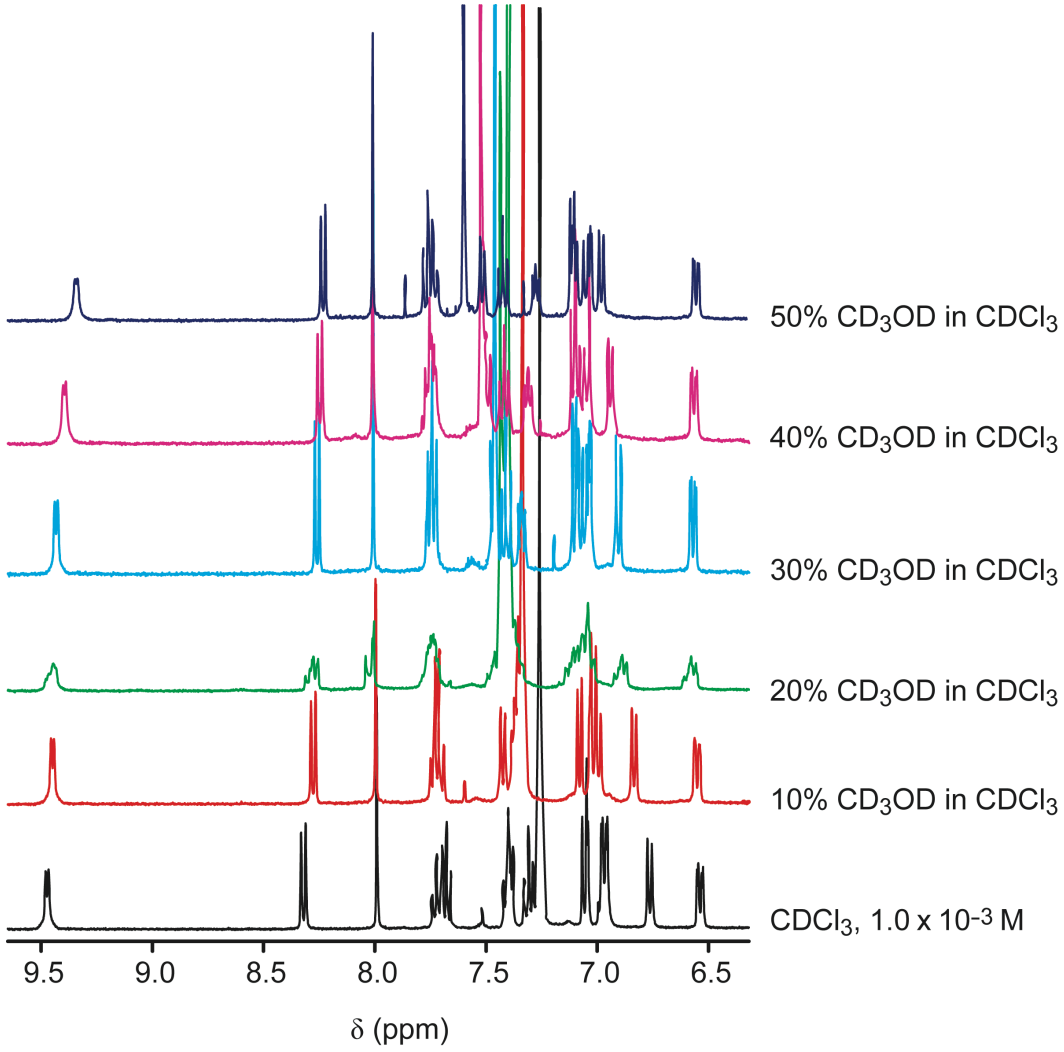
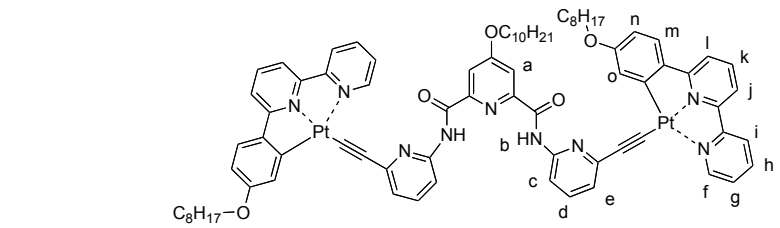


Fig. S6: NMR spectral traces of **DiPt** (1.0 x 10^{-3} M) in $CDCl_3$ at 298 K in the presence of various content of CD_3OD. ((Black) 0%, (red) 10%, (green) 20%, (light blue) 30%, (pink) 40% and (dark blue) 50% of CD_3OD in $CDCl_3$).

Table S6. ^{1}H NMR chemical shift information of **DiPt** (1.0 x 10^{-3} M).

Proton	^{1}H NMR (ppm) $CDCl_3$	^{1}H NMR (ppm) $CD_3OD/CDCl_3$ (1:1)
a	7.98	8.01
b	11.65	11.52 [a]
c	8.31	8.23
d, h	7.69	7.75
e	7.37	7.52
f	9.46	9.35
g	7.39	7.28
i, j, l	7.09-6.91	7.14-7.01
k	7.30	7.42
m	6.75	6.98
n	6.52	6.56
o	7.05	7.03

[a] $CH_3OH/CDCl_3$ (1:1).



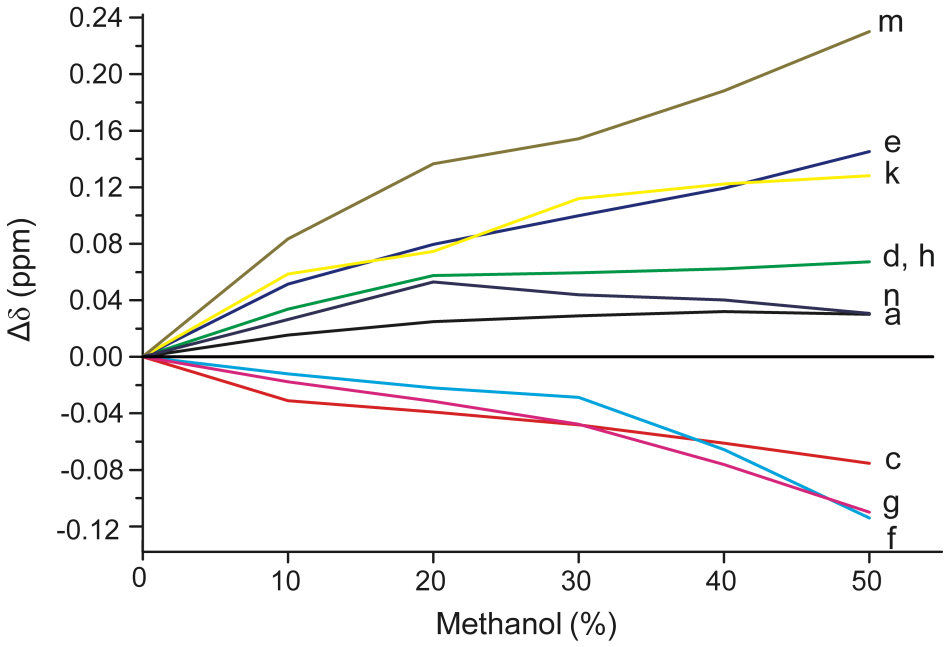


Fig. S7: Plot of the ^{1}H chemical shift alteration, where Δδ (ppm) was plotted against the percentage of CD_3OD of complex **DiPt** (1.0 × 10^{-3} M) in $CDCl_3$ at 295 K; H_i, H_j and H_l: show positive Δδ shift.

The chemical shift was plotted against the methanol concentration revealing a non linear change of the chemical shift. This non linear behaviour was observed especially for the protons of the phenylbipyridine ligand. Strong chemical shift changes were observed at methanol concentrations above 30% CD_3OD in $CDCl_3$. The weak interaction of H_c to the carbonyl oxygen might be present (indicated in Fig. S8) as reported.[4]

This plot supports following methanol induced conformational changes:

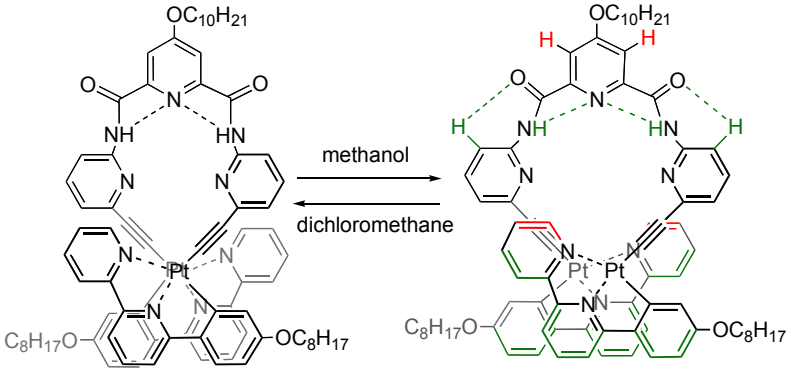


Fig. S8: Proposed methanol induced conformational change of **DiPt**. Red indicates stronger interaction in the presence of methanol, whereas green indicates weaker interaction in the presence of methanol.

IV. Spectra and Figures: Low Temperature Studies

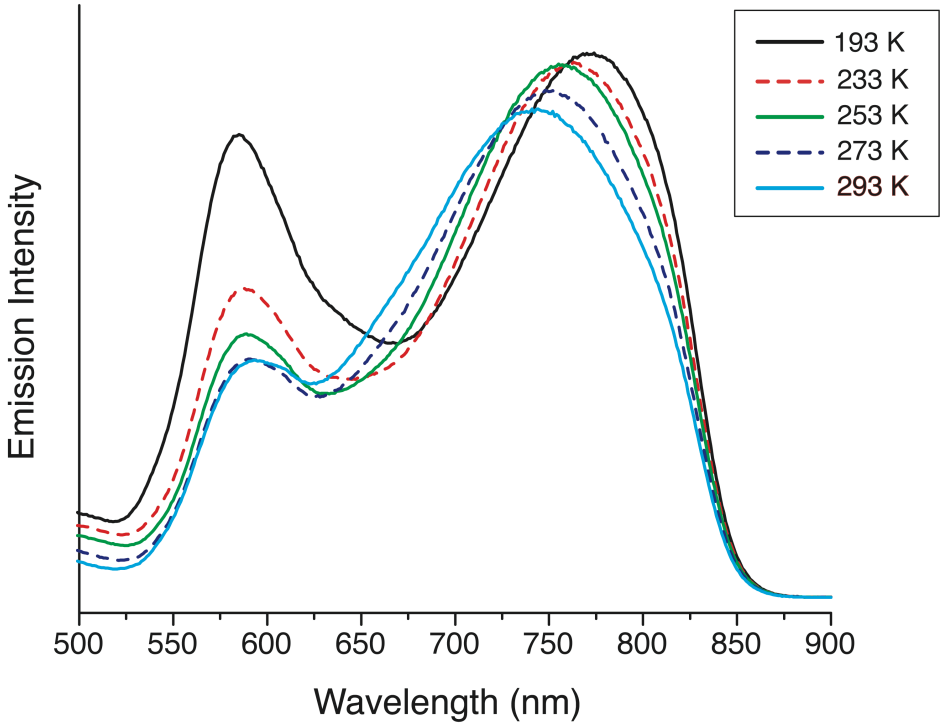


Fig. S9: Emission spectral traces of **DiPt** (2.5 x 10^{-5} M) in dichloromethane at various temperatures, λ_{ex}: 370 nm; (light blue) 293 K, (dark blue) 273 K, (green) 253 K, (red) 233 K, (black) 193 K.

Drastic increase of intensity was observed for the λ_{max} 585 nm emission band by lowering the temperature. This intensity alteration might be either the result of an increased partial π-stack originated by an temperature-dependent increase of the π–π interaction or based on a reduced thermally activated non-radiative decay pathway.

Table S7. λ_{max} of the MMLCT emission band of **DiPt** in CH_2Cl_2 (2.5×10^{-5} M) at various temperatures.

Temp. (K)	λ_{max} (nm)
293	743
273	751
253	756
233	762
193	771

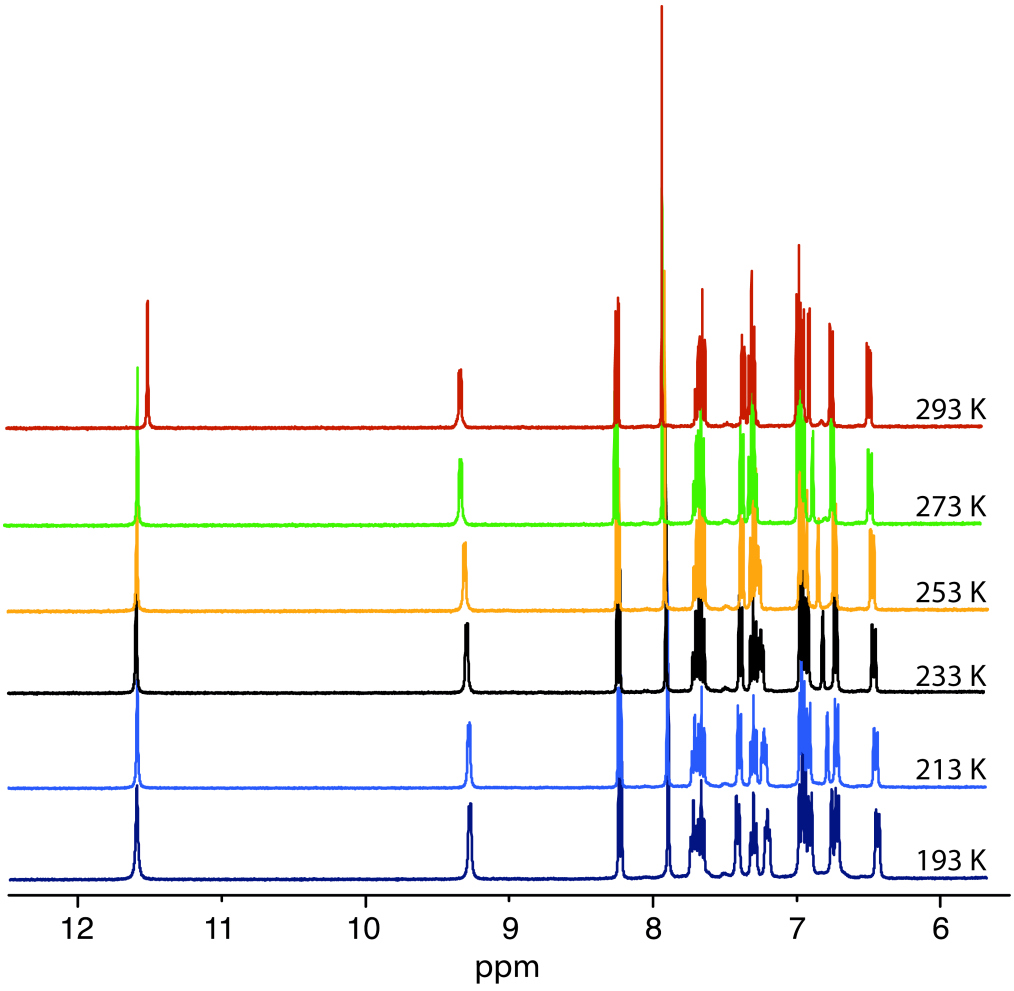
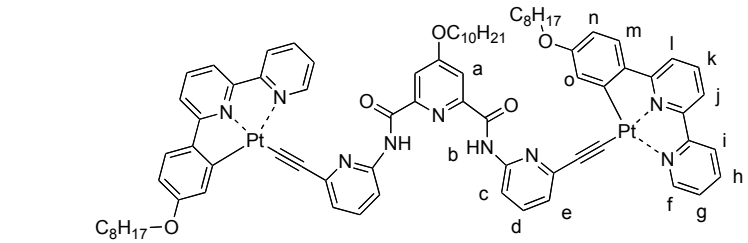


Fig. S10: ^{1}H NMR spectral traces of complex **5** (1.0×10^{-3} M) in CD_2Cl_2 at various temperatures; (red) 293 K , (green) 273 K, (orange) 253 K, (black) 233 K, (light blue) 213 K and (dark blue) 193 K.

Table S8. ^{1}H NMR chemical shift of **DiPt** in CD_2Cl_2 (1.0 x 10^{-3} M).

Proton	293 K (ppm)	193 K (ppm)
a	7.99	7.93
b	11.55	11.62
c	8.30	8.26
d	7.74	7.76
e	7.42	7.45
f	9.39	9.31
g	7.37	7.24
h	7.71	7.70
i	7.05	6.95
k	7.37	7.34
j, l	7.05	7.00
m	6.81	6.76
n	6.55	6.48
o	6.97	6.80



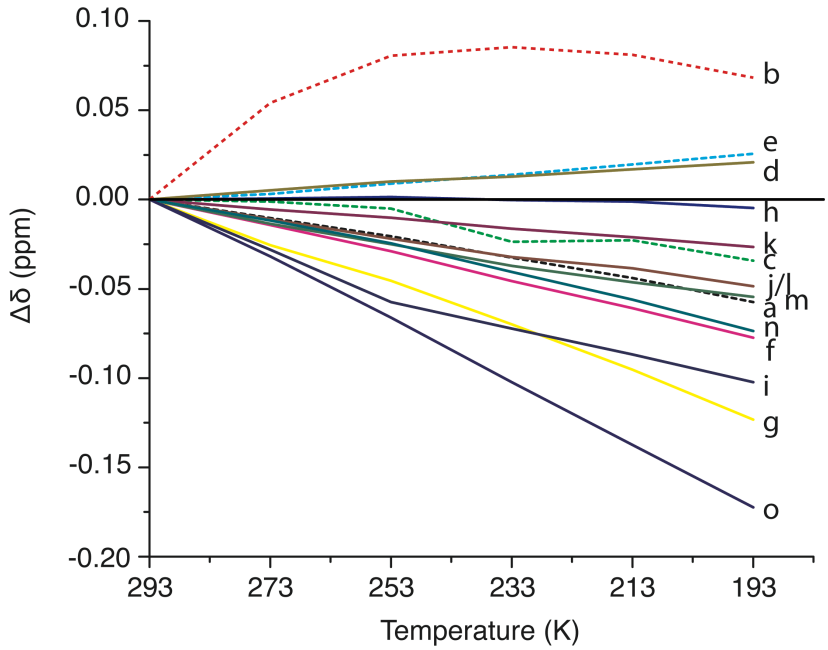


Fig. S11: Plot of the chemical shift alteration of **DiPt** (1.0 × 10^{-3} M in CD_2Cl_2), where Δδ (ppm) was plotted against the decreasing temperature.

Most chemical shift changes are linear in nature, originated by an increasing π–π interaction. Protone H_b reveals non linear shift changes. This change is based on H-bond interactions. The weak interaction of H_c to the carbonyl oxygen might be present (indicated in Fig. S12) as reported.[4]

The plot reveals following conformational changes:

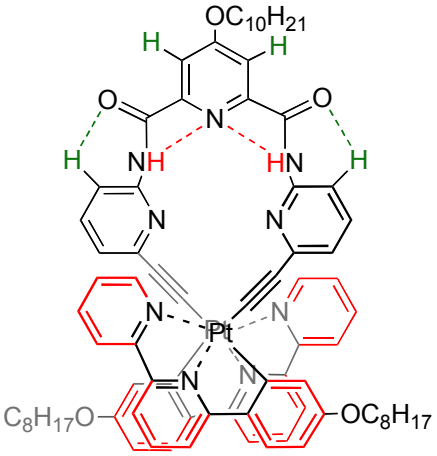


Fig. S12: Proposed temperature induced conformational change of **DiPt**. Red indicates stronger interaction at a lower temperature; Green indicates a weaker interaction at a lower temperature.

V. Spectra and Figures: High Temperature Studies

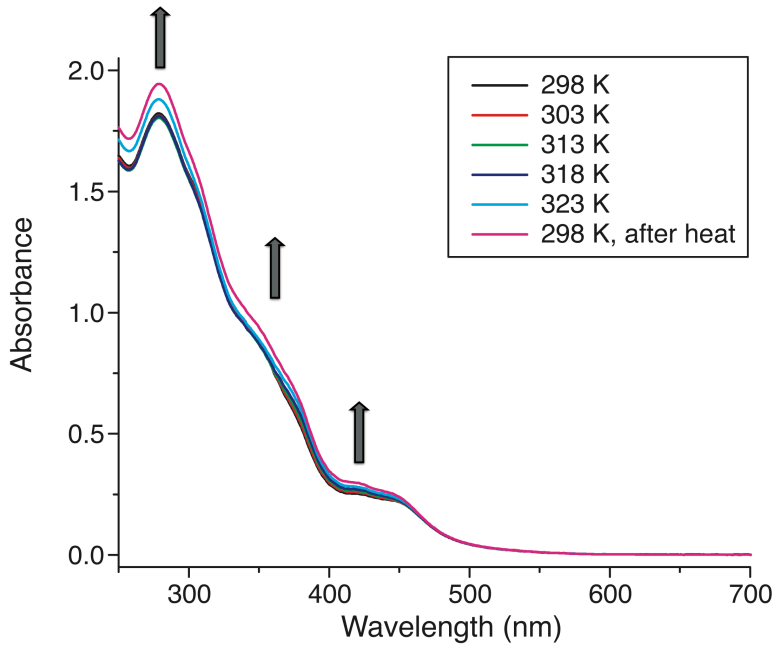


Fig. S13: UV-vis absorption spectral traces of **DiPt** in 1,2-dichloroethane (2.5 x 10^{-5} M), temperature influence measured at (black) 298 K, (red) 303 K, (green) 313 K, (dark blue) 318 K, (light blue) 323 K and (pink) after cooling to 298 K, arrows indicating temperature induced changes in the absorption.

Main changes were observed between 318 K and 323 K. Cooling the sample to 298 K after heat exposure does not result in a reversible behaviour.

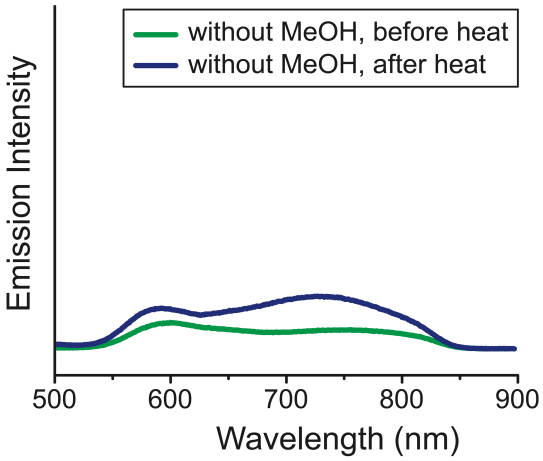


Fig. S14: Emission spectra of **DiPt** (2.5 x 10^{-5} M), λ_{ex}: 380 nm, at 298 K: (green) in 1,2-dichloroethane, (blue) in 1,2-dichloroethane after heating up to 323 K (black).

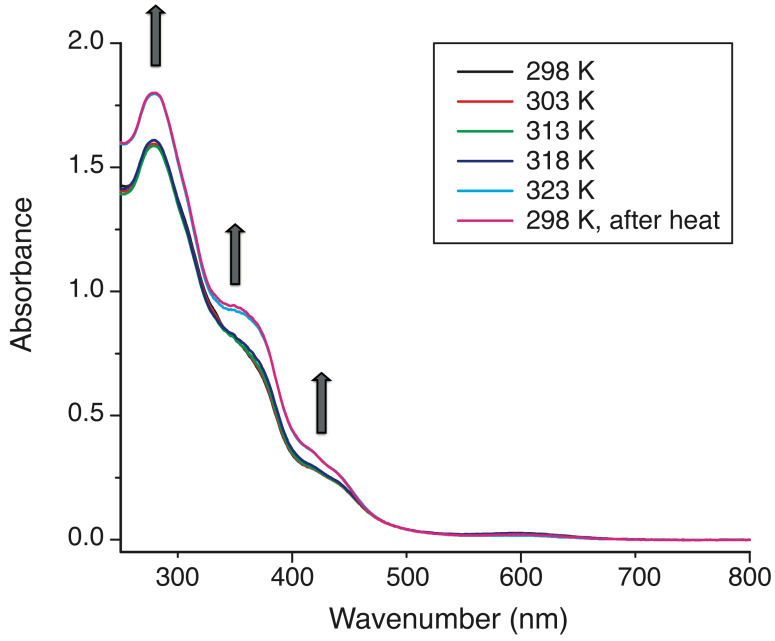


Fig. S15: UV-vis absorption spectral traces of **DiPt** in 10% methanol in 1,2-dichloroethane (2.5 x 10^{-5} M), temperature influence measured at (black) 298 K, (red) 303 K, (green) 313 K, (dark blue) 318 K, (light blue) 323 K and (pink) after cooling to 298 K, arrows indicating temperature induced changes in the absorption.

Main changes were observed between 318 K and 323 K. After heating the sample up to 323 K, it was cooled to 298 K, but UV-vis spectra show no major changes. Therefore, the sample seems to show a non reversible behaviour by only lowering the temperature.

References

1 V. Berl, I. Huc, R. G. Khoury, J.-M. Lehn, *Chem.--Eur. J.*, 2001, **7**, 2798.
2 T. Moriuchi, Y. Sakamoto, S. Noguchi, T. Fujiwara, S. Akine, T. Nabeshima, T. Hirao, *Dalton Trans.*, 2012, **41**, 8524.
3 M. Inouye, T. Miyake, M. Furusyo, H. Nakazumi, *J. Am. Chem. Soc.*, 1995, **117**, 12416.
4 I. Huc, V. Maurizot, H. Gornitzka and J.-M. Leger, *Chem. Commun.*, 2002, 578.