

# **New Class of Highly Solvatochromic Dicyano Rhenate(I) Diimine Complexes – Synthesis, Photophysics and Photocatalysis**

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## **Supplementary Information**

## Experimental

**Materials and Reagents.** 1,10-Phenanthroline (phen), 4,4'-di-*tert*-butyl-2,2'-bipyridine (*t*Bu<sub>2</sub>bpy), potassium cyanide (KCN) and [Re<sub>2</sub>(CO)<sub>10</sub>] were purchased from Aldrich Chemical Company and used without further purification. Re(CO)<sub>5</sub>Br<sup>1</sup> and [Re(CO)<sub>3</sub>(N–N)(CN)]<sup>2</sup> (N–N = phen and *t*Bu<sub>2</sub>bpy) were synthesised according to modified literature procedures for related metal complexes. All solvents were of analytical reagent grade and were used without further purification.

**Physical Measurements and Instrumentation.** Photo-substitution reactions were carried out in a micro-photoreactor using a Pen-ray mercury lamp (11SC–1; λ = 254 nm) as the excitation source.<sup>3</sup> <sup>1</sup>H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me<sub>4</sub>Si). All negative-ion ESI mass spectra were recorded on a PE-SCIEX API 150 EX single quadrupole mass spectrometer. The elemental analyses were performed on an Elementar Vario MICRO Cube elemental analyzer.

Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Solution emission measurements were recorded in the spectral mode of a Edinburgh Instruments LP920-KS using the third harmonic output (355-nm; 6-8 ns fwhm pulse width) of Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd-YAG laser (10 Hz) as the excitation source. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles. Steady state emission and excitation spectra at 77 K were recorded on a Horiba Jobin Yvon Fluorolog-3-TCSPC spectrofluorometer. Measurements of the EtOH–MeOH (4:1, v/v) glass samples at 77 K were carried out with the dilute EtOH–MeOH sample solutions contained in a quartz tube inside a liquid nitrogen-filled quartz optical Dewar flask.

Photocatalytic CO<sub>2</sub>-reduction was carried out in a 3-neck micro-photochemical reactor.<sup>3</sup> A solution of **1** (mM) in 4 ml of DMF/TEOA (5:1 v/v) under an atmosphere of CO<sub>2</sub> was irradiated by a Pen-Ray mercury lamp (11SC-1, 90-0019-01;  $\lambda = 365$  nm) in a water-cooled quartz jacket. The photochemical reactor was connected to an infrared gas cell with 10 cm path length to monitor the formation CO by Perkin Elmer FTIR-1600 spectrophotometer during the photo-excitation.

**X-Ray Crystal Structure Determination.** The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer using graphite monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å). The structure was solved by direct methods employing SHELXL-97 program<sup>4</sup> on PC. Re and many non-H atoms were located according to the direct methods. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program<sup>4</sup> on PC. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97.<sup>4</sup> The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

**Syntheses.** All reactions were carried out under strictly anaerobic condition in an inert atmosphere of argon using standard Schlenk techniques.

*Cis,trans*-K[Re(CO)<sub>2</sub>(CN)<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>bpy)] (**1**): A mixture of [Re(CO)<sub>3</sub>(<sup>t</sup>Bu<sub>2</sub>bpy)(CN)] (100 mg, 0.18 mmol) and KCN (1150 mg, 176 mmol) was dissolved in an argon-degassed mixture of methanol and water (6:1 v/v) (21 ml). The resulting solution was then irradiated with UV light ( $\lambda = 254$  nm) for 7 hours at room temperature using a Pen-Ray mercury lamp (11SC-1) in a water-cooled quartz jacket, during which the solution gradually changed from pale yellow to dark red. After removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane and filtered to remove the excess KCN. The filtrate was then purified by column chromatography on silica gel using dichloromethane/acetone/methanol (5:5:1 v/v/v) as eluent. Analytically pure deep red crystals of **1** were

obtained by slow diffusion of diethyl ether vapour into a concentrated methanolic solution of **1**. Yield: 42 mg, 0.07 mmol; 41%.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 298 K):  $\delta$  1.25 (s, 18H,  $^t$ butyl H's), 7.42 (d, 2H,  $J$  = 5.8 Hz, 5,5'-bipyridyl H's), 8.16 (s, 2H, 3,3'-bipyridyl H's), 8.70 (d, 1H,  $J$  = 5.8 Hz, 6,6'-bipyridyl H's). Negative-ion ESI-MS:  $m/z$  563  $[\text{M}]^-$ . IR (KBr disc,  $\nu/\text{cm}^{-1}$ ): 1821, 1902  $\nu(\text{C}\equiv\text{O})$ ; 2063  $\nu(\text{N}\equiv\text{C})$ . Elemental analyses, Calcd for **1** (found) %: C 43.91 (43.98), H 4.02 (4.15), N 9.31 (9.05).

*Cis,trans*-K $[\text{Re}(\text{CO})_2(\text{CN})_2(\text{phen})]$  (**2**): The complex was synthesised according to a procedure similar to that for **1** except  $[\text{Re}(\text{CO})_3(\text{phen})(\text{CN})]$  (100 mg, 0.21 mmol) was used in place of  $[\text{Re}(\text{CO})_3(^t\text{Bu}_2\text{bpy})(\text{CN})]$  in the ligand substitution reaction. Yield: 41 mg, 0.08 mmol; 38%.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 298 K):  $\delta$  7.73 (dd, 2H,  $J$  = 5.1, 8.2 Hz, 3,8-phenanthrolyl H's), 7.83 (s, 2H, 5,6-phenanthrolyl H's), 8.44 (d, 2H,  $J$  = 8.2 Hz, 4,7-phenanthrolyl H's), 9.22 (d, 2H,  $J$  = 5.1 Hz, 2,9-phenanthrolyl H's). Negative-ion ESI-MS:  $m/z$  476  $[\text{M}]^-$ . IR (KBr disc,  $\nu/\text{cm}^{-1}$ ): 1816, 1917  $\nu(\text{C}\equiv\text{O})$ ; 2050  $\nu(\text{N}\equiv\text{C})$ . Elemental analyses, Calcd for **2**· $\text{CH}_3\text{OH}$  (found) %: C 37.42 (37.73), H 2.22 (2.52), N 10.27 (10.08).

*Cis,trans*- $^n\text{Bu}_4\text{N}[\text{Re}(\text{CO})_2(\text{CN})_2(^t\text{Bu}_2\text{bpy})]$  (**3**): To a suspension of **1** (40 mg, 0.07 mmol) in  $\text{CH}_2\text{Cl}_2$  was added,  $^n\text{Bu}_4\text{NCl}$  (19 mg, 0.07 mmol). The resulting suspension was stirred for an hour and then filtered to remove the KCl precipitate. After removal of the solvent under reduced pressure, deep red crystals of **3** were obtained from slow diffusion of diethyl ether vapour into the concentrated acetone solution of **3**. 48 mg, 0.06 mmol; 89%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  1.01 (t, 12H,  $J$  = 7.4 Hz,  $^n$ butyl H's), 1.37 (s, 18H,  $^t$ butyl H's), 1.46 (sextet, 8H,  $J$  = 7.4 Hz,  $^n$ butyl H's), 1.69 (septet, 8H,  $J$  = 7.4, 8.5 Hz,  $^n$ butyl H's), 3.32 (t, 8H,  $J$  = 8.5 Hz,  $^n$ butyl H's), 7.27 (d, 2H,  $J$  = 5.8 Hz, 5,5'-bipyridyl H's), 7.94 (s, 2H, 3,3'-bipyridyl H's), 8.93 (d, 1H,  $J$  = 5.8 Hz, 6,6'-bipyridyl H's). ESI-MS:  $m/z$  563  $[\text{M}]^-$ . IR (KBr disc,  $\nu/\text{cm}^{-1}$ ): 1828, 1906  $\nu(\text{C}\equiv\text{O})$ ; 2077  $\nu(\text{N}\equiv\text{C})$ . Elemental analyses, Calcd for **3**·0.5 $\text{CH}_3\text{COCH}_3$  (found) %: C 56.87 (56.57), H 7.61 (7.92), N 8.40 (8.26).

*Cis,trans*-<sup>n</sup>Bu<sub>4</sub>N[Re(CO)<sub>2</sub>(CN)<sub>2</sub>(phen)] (**4**): The complex was synthesised according to a procedure similar to that for **3** except **2** (40 mg, 0.08 mmol) was used in place of **1** in the metathesis. Yield: 45 mg, 0.06 mmol; 81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 1.01 (t, 12H, *J* = 7.4 Hz, <sup>n</sup>butyl H's), 1.46 (sextet, 8H, *J* = 7.4 Hz, <sup>n</sup>butyl H's), 1.69 (septet, 8H, *J* = 7.4, 8.5 Hz, <sup>n</sup>butyl H's), 3.37 (t, 8H, *J* = 8.5 Hz, <sup>n</sup>butyl H's), 7.66 (dd, 2H, *J* = 5.0, 8.1 Hz, 3,8-phenanthrolyl H's), 7.91 (s, 2H, 5,6-phenanthrolyl H's), 8.35 (d, 2H, *J* = 8.1 Hz, 4,7-phenanthrolyl H's), 9.38 (d, 2H, *J* = 5.0 Hz, 2,9-phenanthrolyl H's). ESI-MS: *m/z* 476 [M]<sup>-</sup>. IR (KBr disc, *v*/cm<sup>-1</sup>): 1820, 1886 *v*(C≡O); 2073 *v*(N≡C). Elemental analyses, Calcd for **4** (found) %: C 53.61 (53.45), H 6.19 (6.44), N 9.77 (10.02).

**Table S1.** Crystal and structure determination data for **3** and **4**.

	<b>3</b>	<b>4</b>
Formula	C <sub>22</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Re·C <sub>16</sub> H <sub>36</sub> N	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub> Re(H <sub>2</sub> O)·C <sub>16</sub> H <sub>36</sub> N
<i>M<sub>r</sub></i>	805.11	734.94
<i>T</i> / K	133(2)	133(2)
<i>a</i> / Å	15.2908(4)	9.9402(2)
<i>b</i> / Å	12.3356(3)	15.3605(2)
<i>c</i> / Å	21.2687(6)	21.5569(3)
<i>α</i> / deg	90	90
<i>β</i> / deg	101.227(2)	90
<i>γ</i> / deg	90	90
<i>V</i> / Å <sup>3</sup>	3934.96(18)	3291.45(9)
Crystal color	Red	Red
Crystal system	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>Z</i>	4	4
<i>F</i> (000)	1656	1488
<i>D<sub>c</sub></i> / g cm <sup>-3</sup>	1.359	1.483
Crystal dimensions / mm	0.3 × 0.3 × 0.1	0.8 × 0.2 × 0.1
<i>λ</i> / Å (graphite monochromated, Cu-K <sub>α</sub> )	1.5418	1.5418
Absorption coefficient / mm <sup>-1</sup>	6.316	7.521
Collection range	3.27 ≤ <i>θ</i> ≤ 71.67° ( <i>h</i> : -14 to 18; <i>k</i> : -14 to 14; <i>l</i> : -25 to 25)	3.53 ≤ <i>θ</i> ≤ 71.33° ( <i>h</i> : -8 to 11; <i>k</i> : -18 to 17; <i>l</i> : -24 to 26)
Completeness to theta	99.9%	99.8 %
No. of data collected	16058	12936
No. of unique data	7017	5694
No. of data used in refinement, <i>m</i>	6575	5631
No. of parameters refined, <i>p</i>	434	374
<i>R</i> <sup>a</sup>	0.0267	0.0297
<i>wR</i> <sup>a</sup>	0.0753	0.0847
Goodness-of-fit, <i>S</i>	1.031	1.078
Maximum shift, ( <i>Δ</i> / <i>σ</i> ) <sub>max</sub>	0.005	0.001
Residual extrema in final difference map, eÅ <sup>-3</sup>	+3.449, -1.141	+1.140, -0.763

<sup>a</sup>*w* = 1 / [*σ*<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (*ap*)<sup>2</sup> + *bP*], where *P* = [2*F<sub>c</sub>*<sup>2</sup> + Max(*F<sub>o</sub>*<sup>2</sup>, 0)] / 3

**Table S2.** Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for **3** and **4**.

<b>3</b>	Re(1)–C(1)	2.115 (3)	C(3)–O(1)	1.172 (4)
	Re(1)–C(2)	2.097 (3)	C(4)–O(2)	1.174 (4)
	Re(1)–C(3)	1.886 (3)	C(1)–N(1)	1.154 (4)
	Re(1)–C(4)	1.881 (3)	C(2)–N(2)	1.155 (4)
	N(3)–Re(1)–N(4)	74.1 (3)	Re(1)–C(3)–O(1)	176.8 (2)
	Re(1)–C(1)–N(1)	177.0 (3)	Re(1)–C(4)–O(2)	177.2 (2)
	Re(1)–C(2)–N(2)	178.0 (2)		
<b>4</b>	Re(1)–C(1)	2.116 (4)	C(3)–O(2)	1.166 (7)
	Re(1)–C(2)	2.129 (4)	C(4)–O(1)	1.168 (7)
	Re(1)–C(3)	1.897 (6)	C(1)–N(1)	1.114 (7)
	Re(1)–C(4)	1.883 (6)	C(2)–N(2)	1.103 (7)
	N(3)–Re(1)–N(4)	74.95 (16)	Re(1)–C(3)–O(1)	178.3 (6)
	Re(1)–C(1)–N(1)	178.0 (5)	Re(1)–C(4)–O(2)	176.4 (5)
	Re(1)–C(2)–N(2)	175.5 (5)		

**Table S3.** UV-vis absorption data of complexes **1–4** recorded in different solvent media.

	Medium	Absorption $\lambda_{\text{abs}}/ \text{nm}$ ( $\epsilon / \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ )
<b>1</b>	THF	-- <sup>a</sup>
	DMF	292 (16895), 300 (21255), 360 (5075), 491 (3720)
	DMSO	293 (18595), 299 (19085), 360 (3955), 475 (2665)
	CH <sub>2</sub> Cl <sub>2</sub>	245 (10510), 298 (12675), 333 (4520), 450 (2975)
	Acetone	354 (4410), 477 (3115)
	EtOH	243 sh (15685), 290 (19540), 296 (20090), 345 (4725), 457 (3260)
	MeCN	205 (38575), 245 sh (12025), 289 (14295), 298 (17770), 351 (4260), 469 (3145)
	MeOH	245 sh (13865), 296 (19395), 339 (4840), 450 (3525)
	H <sub>2</sub> O	206 (42770), 243 sh (13925), 294 (17430), 400 (3380)
<b>2</b>	THF	-- <sup>a</sup>
	DMF	287 sh (10240), 496(3180)
	DMSO	270 (21880), 291 sh (9115), 480 (2695)
	CH <sub>2</sub> Cl <sub>2</sub>	-- <sup>a</sup>
	Acetone	504 (3050)
	EtOH	225 (29520), 267 (23775), 287 sh (9000), 463 (2570)
	MeCN	199 (37350), 224 (32575), 266 (26085), 287 sh (9780), 472 (2775)
	MeOH	223 (27330), 267 (22630), 285 sh (8385), 455 (2830)
	H <sub>2</sub> O	201 (23415), 222 (18790), 265 (13485), 286 sh (5215), 400 (1905)
<b>3</b>	THF	294 (22510), 300 (22250), 366 (3690), 506 (2660)
	DMF	293 (15622), 299 (19105), 359 (4475), 489 (3260)
	DMSO	300 (17540), 354 (4335), 473 (3180)
	CH <sub>2</sub> Cl <sub>2</sub>	248 sh (11670), 300 (15760), 352 (3910), 476 (2750)
	Acetone	360 (3490), 495 (3210)
	EtOH	244 sh (13760), 289 (15860), 296 (18895), 348 (4715), 459 (3370)
	MeCN	204 (42410), 244 sh (13030), 291 (15470), 297 (18415), 347 (4360), 470 (3175)
	MeOH	241 sh (15740), 295 (20910), 342 (5255), 448 (3815)
	H <sub>2</sub> O	211 (33430), 243 sh (13540), 294 (16960), 402 (3005)
<b>4</b>	THF	-- <sup>a</sup>
	DMF	271(22930), 290 sh (9325), 494 (3890)
	DMSO	271 (20710), 291 sh (9265), 484 (3765)
	CH <sub>2</sub> Cl <sub>2</sub>	270 (20890), 289 sh (7135), 483 (2855)
	Acetone	509 (3505)
	EtOH	224 (30415), 268(26680), 287 sh (8700), 465 (2725)
	MeCN	200 (29690), 224(23400), 268 (20940), 286 sh (7105), 477 (2895)
	MeOH	223(35300), 267 (30650), 286 sh (9965), 457 (4365)
	H <sub>2</sub> O	201(29100), 221 (22680), 267 (17605), 288 sh (5655), 403 (2385)

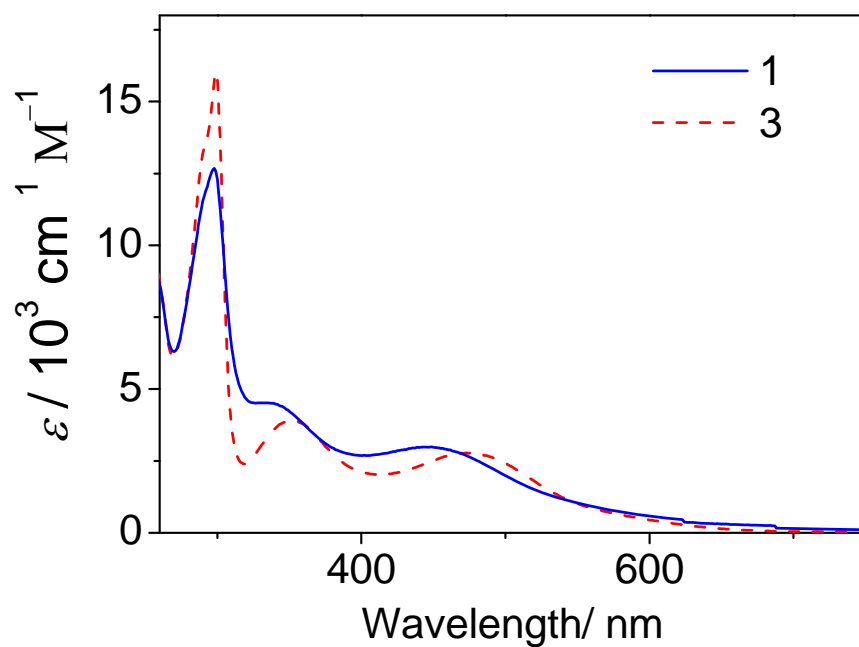
<sup>a</sup>Due to limited solubility, the absorption data cannot be accurately determined.



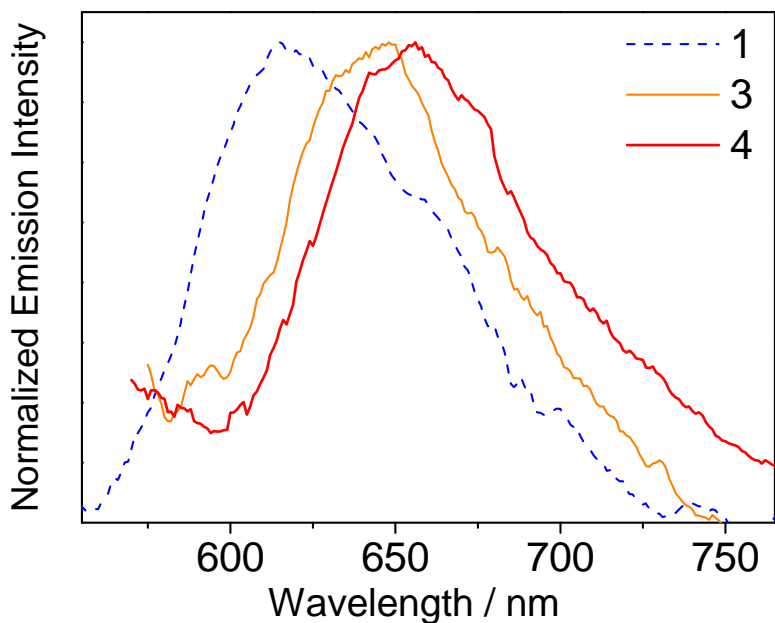
**Table S4.** Emission data of complexes **1–4**.

	Medium (T/K)	Emission $\lambda_{em}/$ nm ( $\tau/\mu$ s)	$\phi_{em}^a$
<b>1</b>	CH <sub>2</sub> Cl <sub>2</sub> (298)	650 (< 0.01)	0.0002
	Glass <sup>b</sup> (77)	620 (0.083)	
<b>2</b>	CH <sub>2</sub> Cl <sub>2</sub> (298)	-- <sup>c</sup>	-- <sup>c</sup>
	Glass <sup>b</sup> (77)	647 (0.14)	
<b>3</b>	CH <sub>2</sub> Cl <sub>2</sub> (298)	667 (< 0.01)	-- <sup>d</sup>
	Glass <sup>b</sup> (77)	638 (0.095)	
<b>4</b>	CH <sub>2</sub> Cl <sub>2</sub> (298)	646 (< 0.01)	-- <sup>d</sup>
	Glass <sup>b</sup> (77)	655 (0.14)	

<sup>a</sup>The luminescence quantum yield with excitation at 436 nm. <sup>b</sup>EtOH/MeOH (4:1 v/v). <sup>c</sup>Due to limited solubility, the emission data cannot be determined. <sup>d</sup>The luminescence quantum yield is  $< 1 \times 10^{-4}$ , which cannot be accurately determined.



**Fig. S1** Overlaid absorption spectra of **1** and **3** in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K.



**Fig. S2** Normalized emission spectra of **1**, **3** and **4** in rigid EtOH/MeOH (4:1, v/v) glassy medium at 77K.

## References:

1. S. P. Schmidt, W. C. Trogler, F. Basolo, M. A. Urbancic and J. R. Shapley, *Inorg. Synth.*, 1990, **28**, 160.
2. R. M. Leasure, L. Sacksteder, D. Nesslerodt, G. A. Reitz, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1991, **30**, 3722.
3. (a) J. H. Penn and R. D. Orr, *J. Chem. Educ.*, 1989, **66**, 86; (b) C.-C. Ko, L. T.-L. Lo, C.-O. Ng and S.-M. Yiu, *Chem. Eur. J.*, 2010, **16**, 13773.
4. SHELX-97, Sheldrick, G. M. (1997). SHELX-97: Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany.