

# New ligands in the 2,2'-dipyridylamine series and their Re(I) complexes; synthesis, structures and luminescence properties

Nail M. Shavaleev,<sup>a</sup> Andrea Barbieri,<sup>b</sup> Zöe R. Bell,<sup>a</sup> Michael D. Ward<sup>\*ac</sup> and Francesco Barigelletti<sup>\*b</sup>

<sup>a</sup> School of Chemistry, University of Bristol, Cantock's Close, Bristol UK BS8 1TS

<sup>b</sup> Istituto ISOF-CNR, Via P. Gobetti 101, 40129, Bologna, Italy. E-mail: franz@isof.cnr.it

<sup>c</sup> Department of Chemistry, University of Sheffield, Brook Hill, Sheffield UK S3 7HF.

E-mail: m.d.ward@sheffield.ac.uk; Fax: 0114 2229346

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A series of new derivatives of the di(2-pyridyl)amine ligand has been prepared, having the general formula (py)<sub>2</sub>NR, where R is one of a wide range of groups including naphthyl, pyrenyl, benzo-18-crown-6, pyrenyl, oxazolyl and bromo-biphenyl. All ligands are luminescent, with emission maxima between 370 and 520 nm, and with quantum yields in fluid solution of up to 0.74. Reaction of these ligands with Re(CO)<sub>5</sub>Cl afforded complexes of the type [Re(CO)<sub>3</sub>ClL] in which the di(2-pyridyl)amine ligand binds as an *N,N*-bidentate chelate via the two pyridyl units; five such complexes have been structurally characterised. With one exception the complexes are essentially non-luminescent, which we ascribe to the energetic availability of metal-based d-d excited states which can quench any MLCT or ligand-centred excited states. The exception is [Re(CO)<sub>3</sub>Cl(tppd)] [where tppd = *N,N,N',N'*-tetrakis(2-pyridyl)-*p*-phenylenediamine] in which one di(2-pyridyl)amine site is occupied by a {Re(CO)<sub>3</sub>Cl} unit but the other is vacant; this luminesces in fluid solution at 516 nm ( $\phi = 0.04$ ,  $\tau = 42$  ns).

## Introduction

Many coordination complexes of 2,2'-dipyridylamine (dpa)<sup>1–7</sup> and its substituted derivatives<sup>8–11</sup> have been prepared and structurally characterised, partly because the different coordination modes available to the ligand result in unusual structural chemistry, and partly because of the luminescence properties of some of the complexes. 2,2'-Dipyridylamine on its own is weakly luminescent,<sup>12</sup> and this is retained in some of its complexes; for example, ligand-based blue fluorescence has been reported for zinc(II)<sup>2</sup> and cadmium(II)<sup>3</sup> complexes of dpa, and also for organoaluminium complexes with deprotonated dpa.<sup>4</sup> Emission from ligand-based or charge-transfer excited states has been observed for complexes of iridium(III),<sup>5</sup> rhodium(III)<sup>5</sup> and ruthenium(II)<sup>6</sup> with neutral or deprotonated dpa.

New materials with improved photophysical properties based on dpa have been prepared by substitution of the amine hydrogen atom with an organic group.<sup>9–11</sup> Using a polyfunctional organic group as a spacer between two or more dpa termini has allowed access to new linear or star-shaped bridging ligands. A variety of such bridging ligands and their mono- and polynuclear complexes with zinc(II), silver(I), platinum(II) and lanthanide(III) ions have recently been synthesized and structurally characterised, and many of these—like the complexes of the parent ligand—show strong blue luminescence.<sup>9–11</sup> Organoboron and organosilicon derivatives, and some zinc(II) and silver(I) complexes of dpa derivatives, show efficient blue luminescence as solids and in solution, while their lanthanide(III) tris- $\beta$ -diketonate complexes show sensitized lanthanide(III) emission in the solid state. 2,2'-Dipyridylamine derivatives have been used as blue emitters in electroluminescent devices,<sup>10</sup> and a luminescent sensor for benzene based on the zinc(II) complex of 1,3,5-tris[*p*-(2,2'-dipyridylamino)-phenyl]benzene has been reported.<sup>11</sup>

In this paper we report the syntheses, characterisation, crystal structures and luminescence properties of a series of new

dpa derivatives of dpa with a variety of substituents attached to the amine N atom. These substituents include strongly fluorescent aromatic chromophores such as naphthlene or pyrene, and in one case an 18-crown-6 macrocyclic unit which could be used for additional metal-ion binding. Complexes of these ligands with {Re(CO)<sub>3</sub>Cl} units are also described in this paper, including their structures and luminescence properties. Such rhenium(I) carbonyl complexes with diimine-type ligands often show visible luminescence originating from a metal-to-ligand charge-transfer excited state,<sup>13–15</sup> which has been exploited for development of sensors and luminescent labels,<sup>16</sup> and in electroluminescent materials.<sup>17</sup> It was reported recently that Re(CO)<sub>5</sub>Cl does not react with dpa in solution or in a melt, and that a reaction takes place only in the presence of PPh<sub>3</sub> to give the complex [Re(CO)<sub>2</sub>(PPh<sub>3</sub>)(dpa)Cl].<sup>7</sup> However we have found that dpa derivatives easily react with Re(CO)<sub>5</sub>Cl to give the expected [Re(CO)<sub>3</sub>Cl(NN)] adducts described here. It should be noted that some rhenium(III) and rhenium(VII) complexes of the related ligand tris(2-pyridyl)amine have also been studied.<sup>8a</sup>

## Experimental

### General details

2,2'-Dipyridylamine, other organic reagents, and Re(CO)<sub>5</sub>Cl were obtained from Aldrich or Lancaster Synthesis and used without further purification. The following instrumentation was used for routine spectroscopic characterisation: UV/Vis spectra, a Perkin-Elmer Lambda 2 spectrophotometer; <sup>1</sup>H NMR spectra, a Jeol GX-270 spectrometer at 270 MHz; EI and FAB mass spectra, a VG-Autospec spectrometer.

### Syntheses of 2,2'-dipyridylamine derivatives<sup>9,10</sup>

**Method 1.** A solid mixture of dpa, the appropriate bromo-aromatic derivative, KOH (excess, 1.5 equiv, compared to of

dpa) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (catalytic amount) under  $\text{N}_2$  was heated at  $180^\circ\text{C}$  for 6 h during which time it melted and then re-solidified. Specific quantities for each reaction are given below; one of the two components (the dpa or the bromo-aromatic) was used in excess according to which was more soluble in EtOH; the residue of that component was easily removed at the end of the reaction during recrystallisation from EtOH. The reaction mixture was cooled and partitioned between water and dichloromethane, with the final pH of the aqueous phase adjusted to 6.5–7 using acetic acid or  $\text{NaHCO}_3$ . The organic phase was separated, dried with  $\text{MgSO}_4$ , and the solvent removed under reduced pressure. The crude product was purified by column chromatography on alumina on a short column eluting with  $\text{CH}_2\text{Cl}_2$ , or acetone/ $\text{CH}_2\text{Cl}_2$ . The chromatography was followed with the use of a hand-held UV lamp (365 nm); the main fraction showing blue luminescence was collected, evaporated to dryness, and recrystallized twice from a small amount of boiling ethanol. The solid was washed with cold ethanol and hexane and dried under vacuum. This procedure usually gave analytically pure product, however in some cases additional column chromatography was required which was carried out on alumina eluting with  $\text{CH}_2\text{Cl}_2$ , or acetone/ $\text{CH}_2\text{Cl}_2$ .

**Method 2.** A solution of dpa and the appropriate bromo-aromatic derivative in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ; see below for quantities of reagents) was mixed with a solution of  $\text{K}_2\text{CO}_3$  (1 equiv. with respect to dpa) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (catalytic amount) in water (10  $\text{cm}^3$ ). The resulting biphasic mixture was evaporated to dryness and further dried under vacuum; this procedure ensures thorough mixing of components. The resulting solid mixture was heated under  $\text{N}_2$  at  $180^\circ\text{C}$  for 6 h, and worked up as described in method 1 above.

All new dpa derivatives were obtained as air- and moisture-stable white or pale yellow solids which were soluble in chlorinated solvents, arenes, and boiling ethanol, but insoluble in hexane and cold ethanol.

**TPPD,<sup>9b</sup> 2-TPA<sup>8a</sup> and 3-TPA** were synthesized according to the literature methods.

**BPBr.** This ligand was obtained as a by-product in the synthesis of *N,N,N',N'*-tetra(2-pyridyl)biphenyl-4,4'-diamine according to the literature method.<sup>9b</sup> Anal. calc. for  $\text{C}_{22}\text{H}_{16}\text{BrN}_3$ : C, 65.7; H, 4.0; N, 10.5. Found: C, 66.1; H, 4.3; N, 9.9%. EI MS:  $m/z$  402 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.35 (2H, d; pyridyl  $\text{H}^6$ ), 7.5–7.6 (6H, m; pyridyl  $\text{H}^4$  and two pairs of phenyl H), 7.45 (2H, d; phenyl), 7.24 (2H, d; phenyl), 7.05 (2H, d; pyridyl  $\text{H}^3$ ), 6.95 (2H, ddd; pyridyl  $\text{H}^5$ ).

**NAP.** This was prepared from dpa (3.03 g, 17.7 mmol), 2-bromonaphthalene (3.94 g, 19.0 mmol), KOH (1.40 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.075 g) by method 1, which gave 1.24 g (23%) of the product. Anal. calc. for  $\text{C}_{20}\text{H}_{15}\text{N}_3$ : C, 80.8; H, 5.1; N, 14.1. Found: C, 81.7; H, 5.4; N, 14.2%. EI MS:  $m/z$  296 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.34 (2H, d; pyridyl  $\text{H}^6$ ), 7.8–7.9 (2H, m; naphthyl), 7.69 (1H, m; naphthyl), 7.52–7.62 (3H, m; pyridyl  $\text{H}^4$  and one naphthyl H), 7.42 (2H, m; naphthyl), 7.33 (1H, dd; naphthyl), 7.05 (2H, d; pyridyl  $\text{H}^3$ ), 6.95 (2H, ddd; pyridyl  $\text{H}^5$ ).

**NMe.** This was prepared from dpa (3.03 g, 17.7 mmol), 4-bromo-*N,N*-dimethylaniline (3.80 g, 19.0 mmol), KOH (1.40 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.075 g) by method 1, which gave 1.055 g (21%) of the product. The green-blue oil obtained after column chromatography was sonicated with hexane to give a dark red solution and a pale-green solid: the solid was filtered off and recrystallized twice from a small amount of ethanol

washing the product on filter each time with cold ethanol and hexane. Anal. calc. for  $\text{C}_{18}\text{H}_{18}\text{N}_4$ : C, 74.5; H, 6.3; N, 19.3. Found: C, 74.7; H, 6.6; N, 19.4%. EI MS:  $m/z$  290 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.30 (2H, d; pyridyl  $\text{H}^6$ ), 7.49 (2H, td; pyridyl  $\text{H}^4$ ), 7.10 (2H, d; phenyl), 6.96 (2H, d; pyridyl  $\text{H}^3$ ), 6.85 (2H, ddd; pyridyl  $\text{H}^5$ ), 6.75 (2H, d; phenyl), 2.97 (6H, s;  $\text{NMe}_2$ ).

**DP18C6.** This was prepared from dpa (1.97 g, 11.5 mmol), 4'-bromobenzo-18-crown-6 (3.0 g, 7.7 mmol),  $\text{K}_2\text{CO}_3$  (1.59 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.20 g) by method 2, which gave 2.18 g (59%) of the product. Anal. calc. for  $\text{C}_{26}\text{H}_{31}\text{N}_3\text{O}_6$ : C, 64.9; H, 6.5; N, 8.7. Found: C, 65.1; H, 6.7; N, 8.8%. EI MS:  $m/z$  481 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.30 (2H, d; pyridyl  $\text{H}^6$ ), 7.52 (2H, td; pyridyl  $\text{H}^4$ ), 6.96 (2H, d; pyridyl  $\text{H}^3$ ), 6.88 (3H, m; pyridyl  $\text{H}^5$  and one phenyl H), 6.75 (2H, m; phenyl), 4.17 (2H, t;  $\text{CH}_2$ ), 4.06 (2H, t;  $\text{CH}_2$ ), 3.93 (2H, t;  $\text{CH}_2$ ), 3.87 (2H, t;  $\text{CH}_2$ ), 3.68–3.82 (12H, m; 6  $\text{CH}_2$  groups).

**2NDPA.** This was prepared from dpa (3.60 g, 21.0 mmol), 2,8-dibromonaphthalene (1.00 g 3.5 mmol),  $\text{K}_2\text{CO}_3$  (2.42 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.1 g) by method 2, which gave 0.43 g (27%) of the product. Anal. calc. for  $\text{C}_{30}\text{H}_{22}\text{N}_6$ : C, 77.2; H, 4.8; N, 18.0. Found: C, 76.6; H, 5.0; N, 17.9%. EIMS:  $m/z$  466 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.34 (4H, d; pyridyl  $\text{H}^6$ ), 7.70 (2H, d; naphthyl), 7.57 (6H, m; pyridyl  $\text{H}^4$  and two naphthyl H), 7.29 (2H, dd; naphthyl), 7.03 (4H, d; pyridyl  $\text{H}^3$ ), 6.94 (4H, ddd; pyridyl  $\text{H}^5$ ).

**DPAPYR.** This was prepared from dpa (1.83 g, 10.7 mmol), 1-bromopyrene (1.0 g, 3.6 mmol),  $\text{K}_2\text{CO}_3$  (2.5 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.1 g) by method 2, which gave 0.27 g (21%) of the product. Anal. calc. for  $\text{C}_{26}\text{H}_{17}\text{N}_3$ : C, 84.1; H, 4.6; N, 11.3. Found: C, 83.9; H, 4.6; N, 11.4%. EIMS:  $m/z$  371 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.31 (2H, d; pyridyl  $\text{H}^6$ ), 7.9–8.3 (9H, m; pyrene); 7.49 (2H, td; pyridyl  $\text{H}^4$ ), 6.95 (2H, d; pyridyl  $\text{H}^3$ ), 6.88 (2H, m; pyridyl  $\text{H}^5$ ).

**XIP.** This was prepared from dpa (1.71 g, 10.0 mmol), 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (1.0 g, 3.3 mmol),  $\text{K}_2\text{CO}_3$  (2.3 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.1 g) by method 2, which gave 0.79 g (60%) of the product. Anal. calc. for  $\text{C}_{24}\text{H}_{17}\text{N}_5\text{O}$ : C, 73.5; H, 4.4; N, 17.9. Found: C, 74.1; H, 4.2; N, 18.0%. EIMS:  $m/z$  390 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.38 (2H, d; pyridyl  $\text{H}^6$ ), 8.06–8.18 (4H, m; phenyl); 7.64 (2H, td; pyridyl  $\text{H}^4$ ), 7.53 (3H, m; phenyl), 7.29 (2H, d; phenyl), 7.07 (2H, d; pyridyl  $\text{H}^3$ ); 7.02 (2H, ddd; pyridyl  $\text{H}^5$ ).

**XIN.** This was prepared from dpa (2.50 g, 14.6 mmol), 2-(4-bromophenyl)-5-(1-naphthyl)-1,3,4-oxadiazole (2.0 g, 5.7 mmol),  $\text{K}_2\text{CO}_3$  (2.5 g) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.1 g) by method 2, which gave 2.22 g (88%) of the product. Anal. calc. for  $\text{C}_{28}\text{H}_{19}\text{N}_5\text{O}$ : C, 76.2; H, 4.3; N, 15.9. Found: C, 76.4; H, 4.6; N, 16.1%. EIMS:  $m/z$  440 (100%,  $M^+$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  9.28 (1H, d; naphthyl), 8.39 (2H, d; pyridyl  $\text{H}^6$ ), 8.27 (1H, d; naphthyl), 8.16 (2H, d; phenyl), 8.05 (1H, d; naphthyl), 7.95 (1H, d; naphthyl), 7.58–7.75 (5H, m; pyridyl  $\text{H}^4$  and three naphthyl H), 7.32 (2H, d; phenyl), 7.08 (2H, d; pyridyl  $\text{H}^3$ ); 7.03 (2H, ddd; pyridyl  $\text{H}^5$ ).

#### Synthesis of rhenium(I) complexes with 2,2'-dipyridylamine derivatives

The complexes were prepared by refluxing  $\text{Re}(\text{CO})_5\text{Cl}$  and the appropriate ligand, in a 1:1 molar ratio (or, in some cases, using excess of ligand) in degassed toluene (30  $\text{cm}^3$ ) for 24 h under  $\text{N}_2$ . In the course of the reaction the solution changed its colour to pale yellow and a white/yellow precipitate

formed. The reaction mixture was evaporated to dryness; the residue was purified by column chromatography on alumina eluting with CH<sub>2</sub>Cl<sub>2</sub>, unless stated otherwise. The chromatography was followed with the use of a hand-held UV lamp (365 nm). The fraction containing the product (non-luminescent, unless stated otherwise) was collected, reduced in volume and the complex precipitated by addition of hexane; the product was filtered off, washed with hexane and ether, and finally dried under vacuum. All new complexes are air- and moisture-stable white solids which are soluble in acetone, chlorinated solvents and tetrahydrofuran, but insoluble in hexane and ether.

**[Re(CO)<sub>3</sub>Cl(TPPD)].** Re(CO)<sub>5</sub>Cl (105 mg, 0.29 mmol) and TPPD (230 mg, 0.55 mmol) gave 120 mg (57%) of the product which was eluted as a yellow-green luminescent fraction. Anal. calc. for C<sub>29</sub>H<sub>20</sub>ClN<sub>6</sub>O<sub>3</sub>Re: C, 48.2; H, 2.8; N, 11.6. Found: C, 48.7; H, 2.5; N, 11.2%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2023, 1917, 1889. FAB MS: *m/z* 723 (55%, {*M*<sup>+</sup>}), 687 (35%, {*M*-Cl}<sup>+</sup>).

**[Re(CO)<sub>3</sub>Cl(2-TPA)].** Re(CO)<sub>5</sub>Cl (104 mg, 0.29 mmol) and 2-TPA (78 mg, 0.31 mmol) gave 125 mg (78%) of the product. Anal. calc. for C<sub>18</sub>H<sub>12</sub>ClN<sub>4</sub>O<sub>3</sub>Re: C, 39.0; H, 2.2; N, 10.1. Found: C, 38.9; H, 2.0; N, 9.7%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2024, 1919, 1897. FABMS: *m/z* 577 (3%, {*M*+Na}<sup>+</sup>), 554 (18%, *M*<sup>+</sup>), 526 (12%, {*M*-CO}<sup>+</sup>), 519 (100%, {*M*-Cl}<sup>+</sup>), 498 (22%, {*M*-2CO}<sup>+</sup>), 470 (10%, {*M*-3CO}<sup>+</sup>).

**[Re(CO)<sub>3</sub>Cl(3-TPA)].** Re(CO)<sub>5</sub>Cl (100 mg, 0.28 mmol) and 3-TPA (73 mg, 0.29 mmol) gave 20 mg (14%) of the product which was eluted with acetone/CH<sub>2</sub>Cl<sub>2</sub> (starting with 0/100 v/v and changing gradually to 5/95 v/v). Anal. calc. for C<sub>18</sub>H<sub>12</sub>ClN<sub>4</sub>O<sub>3</sub>Re: C, 39.0; H, 2.2; N, 10.1. Found: C, 39.5; H, 2.3; N, 9.8%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2024, 1920, 1894. FABMS: *m/z* 577 (9%, {*M*+Na}<sup>+</sup>), 555 (7%, *M*<sup>+</sup>), 519 (12%, {*M*-Cl}<sup>+</sup>).

**[Re(CO)<sub>3</sub>Cl(NAP)].** Re(CO)<sub>5</sub>Cl (100 mg, 0.28 mmol) and NAP (83 mg, 0.28 mmol) gave 80 mg (48%) of the product. Anal. calc. for C<sub>23</sub>H<sub>15</sub>ClN<sub>3</sub>O<sub>3</sub>Re: C, 45.8; H, 2.5; N, 7.0. Found: C, 45.4; H, 2.4; N, 6.9%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2023, 1917, 1889. FABMS: *m/z* 626 (12%, {*M*+Na}<sup>+</sup>), 603 (50%, *M*<sup>+</sup>), 576 (12%, {*M*-CO}<sup>+</sup>), 569 (100%, {*M*-Cl}<sup>+</sup>), 519 (20%, {*M*-3CO}<sup>+</sup>).

**[Re(CO)<sub>3</sub>Cl(BPBr)].** Re(CO)<sub>5</sub>Cl (0.28 mmol) and BPBr (111 mg, 0.28 mmol) gave 144 mg (74%) of the product. Anal. calc.

for C<sub>25</sub>H<sub>16</sub>BrClN<sub>3</sub>O<sub>3</sub>Re: C, 42.4; H, 2.3; N, 5.9. Found: C, 42.4; H, 2.2; N, 5.5%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2023, 1917, 1889. FABMS: *m/z* 730 (10%, {*M*+Na}<sup>+</sup>), 707 (50%, *M*<sup>+</sup>), 679 (14%, {*M*-CO}<sup>+</sup>), 672 (100%, {*M*-Cl}<sup>+</sup>), 623 (24%, {*M*-3CO}<sup>+</sup>).

**[Re(CO)<sub>3</sub>Cl(NMe)].** Re(CO)<sub>5</sub>Cl (100 mg, 0.28 mmol) and NMe (80 mg, 0.28 mmol) gave 117 mg (71%) of the product. Anal. calc. for C<sub>21</sub>H<sub>18</sub>ClN<sub>4</sub>O<sub>3</sub>Re: C, 42.3; H, 3.0; N, 9.4. Found: C, 42.5; H, 3.0; N, 9.5%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2022, 1915, 1888. FABMS: *m/z* 619 (50%, {*M*+Na}<sup>+</sup>), 596 (13%, {*M*<sup>+</sup>}), 561 (95%, {*M*-Cl}<sup>+</sup>).

**[Re(CO)<sub>3</sub>Cl(DP18C6)].** Re(CO)<sub>5</sub>Cl (100 mg, 0.28 mmol) and DP18C6 (133 mg, 0.28 mmol) gave 122 mg (56%) of the product which was eluted with acetone/CH<sub>2</sub>Cl<sub>2</sub> (starting with 0/100 v/v and changing gradually to 50/50 v/v) as a yellow-green-luminescent fraction. The product is only slightly soluble in THF. Anal. calc. for C<sub>29</sub>H<sub>31</sub>ClN<sub>3</sub>O<sub>9</sub>Re: C, 44.2; H, 4.0; N, 5.3. Found: C, 44.6; H, 3.1; N, 4.8%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2022, 1916, 1886. FABMS: *m/z* 810 (30%, {*M*+Na}<sup>+</sup>), 787 (25%, {*M*<sup>+</sup>}), 752 (100%, {*M*-Cl}<sup>+</sup>), 703 (15%, {*M*-3CO}<sup>+</sup>).

### X-ray crystallography

X-Ray quality crystals were grown for [Re(CO)<sub>3</sub>Cl(2-TPA)] and [Re(CO)<sub>3</sub>Cl(3-TPA)] by slow evaporation from a CH<sub>2</sub>Cl<sub>2</sub>/hexane solution of each complex; for [Re(CO)<sub>3</sub>Cl(NMe)] and [Re(CO)<sub>3</sub>Cl(NAP)] by slow evaporation of a THF/heptane solution; and for [Re(CO)<sub>3</sub>Cl(DP18C6)] by slow cooling of a hot THF solution of the complex. For each complex a suitable crystal was coated with hydrocarbon oil and attached to the tip of a glass fibre, which was then transferred to a Bruker-AXS SMART or APEX diffractometer under a stream of cold N<sub>2</sub> at 173 K (SMART instrument) or 100 K (APEX instrument). Details of the crystal parameters, data collection and refinement for each of the structures are collected in Table 1. After data collection, in each case an empirical absorption correction (SADABS) was applied,<sup>18</sup> and the structures were then solved by conventional direct methods and refined on all *F*<sup>2</sup> data using the SHELX suite of programs.<sup>19</sup> In all cases non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters which were *ca.* 1.2x (aromatic CH) or 1.5x (Me) the equivalent isotropic thermal parameters of their parent carbon atoms. The refinements proceeded smoothly

**Table 1** Crystallographic data.<sup>a</sup>

Compound	[Re(CO) <sub>3</sub> Cl(2-TPA)]	[Re(CO) <sub>3</sub> Cl(3-TPA)]	[Re(CO) <sub>3</sub> Cl(NMe)]	[Re(CO) <sub>3</sub> Cl(DP18C6)]·C <sub>4</sub> H <sub>8</sub> O	[Re(CO) <sub>3</sub> Cl(NAP)]
Empirical formula	C <sub>18</sub> H <sub>12</sub> ClN <sub>4</sub> O <sub>3</sub> Re	C <sub>18</sub> H <sub>12</sub> ClN <sub>4</sub> O <sub>3</sub> Re	C <sub>21</sub> H <sub>18</sub> ClN <sub>4</sub> O <sub>3</sub> Re	C <sub>33</sub> H <sub>39</sub> ClN <sub>3</sub> O <sub>10</sub> Re	C <sub>23</sub> H <sub>15</sub> ClN <sub>3</sub> O <sub>3</sub> Re
Formula weight	553.97	553.97	596.05	859.32	603.03
System, space group	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$	monoclinic, <i>P</i> <sub>2</sub> /n	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$
<i>T</i> , K	100(2)	100(2)	173(2)	100(2)	100(2)
<i>a</i> , Å	10.975(2)	11.125(4)	9.1998(15)	11.170(4)	12.1864(13)
<i>b</i> , Å	13.661(2)	14.259(4)	21.486(4)	11.937(4)	13.9338(15)
<i>c</i> , Å	14.578(3)	14.454(6)	21.451(4)	16.536(5)	14.076(2)
$\alpha$ , deg	107.544(15)	98.149(15)	90	74.20(3)	61.504(12)
$\beta$ , deg	111.036(13)	111.39(2)	93.700(4)	80.21(4)	85.830(8)
$\gamma$ , deg	102.713(17)	112.669(15)	90	62.56(2)	79.965(9)
<i>V</i> , Å <sup>3</sup>	1808.1(6)	1860.5(11)	4231.3(12)	1880.3(11)	2068.3(5)
<i>Z</i>	4	4	8	2	4
Calcd density, Mg m <sup>-3</sup>	2.035	1.978	1.871	1.518	1.937
Data/restraints/parameters	8268, 0, 487	8189, 0, 481	9673, 0, 545	8612, 0, 433	9457, 0, 559
$\mu$ (mm <sup>-1</sup> )	6.895	6.701	5.900	3.357	6.036
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0322, 0.0650	0.0481, 0.1146	0.0274, 0.0534	0.0371, 0.0743	0.0259, 0.0561

<sup>a</sup> Data in common:  $\lambda$  = 0.71073 Å. <sup>b</sup> The value of *R*1 is based on selected data with *I* > 2 $\sigma$ (*I*); the value of *wR*2 is based on all data.



**Table 2** Selected bond distances (Å) and angles (°) for the new structures

<b>[Re(CO)<sub>3</sub>Cl(2-TPA)]</b>			
Re(1)–C(51)	1.897(5)	Re(2)–C(161)	1.904(5)
Re(1)–C(61)	1.922(5)	Re(2)–C(141)	1.909(5)
Re(1)–C(41)	1.925(5)	Re(2)–C(151)	1.912(5)
Re(1)–N(11)	2.194(4)	Re(2)–N(121)	2.195(4)
Re(1)–N(21)	2.210(4)	Re(2)–N(111)	2.198(4)
Re(1)–Cl(1)	2.4706(13)	Re(2)–Cl(2)	2.4759(15)
N(11)–Re(1)–N(21)	80.26(14)	N(121)–Re(2)–N(111)	81.79(14)
C(12)–N(1)–C(22)	118.2(4)	C(132)–N(2)–C(122)	117.8(4)
C(12)–N(1)–C(32)	118.0(4)	C(132)–N(2)–C(112)	123.6(4)
C(22)–N(1)–C(32)	123.7(4)	C(122)–N(2)–C(112)	117.6(4)
Py1/py2 <sup>a</sup>	58.0	Py1/py2 <sup>a</sup>	58.7
substituent <sup>b</sup>	10.4	substituent <sup>b</sup>	15.3
<b>[Re(CO)<sub>3</sub>Cl(3-TPA)]</b>			
Re(1)–C(41)	1.895(10)	Re(2)–C(151)	1.897(9)
Re(1)–C(61)	1.907(9)	Re(2)–C(161)	1.910(10)
Re(1)–C(51)	1.911(9)	Re(2)–C(141)	1.939(8)
Re(1)–N(11)	2.194(6)	Re(2)–N(111)	2.188(7)
Re(1)–N(21)	2.201(6)	Re(2)–N(121)	2.200(7)
Re(1)–Cl(1)	2.479(2)	Re(2)–Cl(2)	2.466(2)
N(11)–Re(1)–N(21)	80.8(2)	N(111)–Re(2)–N(121)	81.8(2)
C(33)–N(1)–C(22)	121.0(6)	C(133)–N(2)–C(122)	126.3(7)
C(33)–N(1)–C(12)	122.1(6)	C(133)–N(2)–C(112)	116.8(7)
C(22)–N(1)–C(12)	116.0(6)	C(122)–N(2)–C(112)	116.0(7)
Py1/py2 <sup>a</sup>	61.4	Py1/py2 <sup>a</sup>	60.1
substituent <sup>b</sup>	7.4	substituent <sup>b</sup>	19.9
<b>[Re(CO)<sub>3</sub>Cl(NMe)]</b>			
Re(1)–C(61)	1.905(4)	Re(2)–C(161)	1.912(4)
Re(1)–C(71)	1.906(4)	Re(2)–C(171)	1.914(4)
Re(1)–C(51)	1.907(5)	Re(2)–C(151)	1.932(4)
Re(1)–N(11)	2.178(3)	Re(2)–N(121)	2.188(3)
Re(1)–N(21)	2.182(3)	Re(2)–N(111)	2.191(3)
Re(1)–Cl(1)	2.4666(11)	Re(2)–Cl(2)	2.4765(10)
N(11)–Re(1)–N(21)	79.89(12)	N(121)–Re(2)–N(111)	79.29(11)
C(22)–N(31)–C(12)	122.7(3)	C(112)–N(131)–C(122)	124.3(3)
C(22)–N(31)–C(31)	117.4(3)	C(112)–N(131)–C(131)	116.2(3)
C(12)–N(31)–C(31)	116.8(3)	C(122)–N(131)–C(131)	117.4(3)
Py1/py2 <sup>a</sup>	41.6	Py1/py2 <sup>a</sup>	39.2
substituent <sup>b</sup>	89.5	substituent <sup>b</sup>	88.1
<b>[Re(CO)<sub>3</sub>Cl(DP18C6)]·C<sub>4</sub>H<sub>8</sub>O</b>			
Re(1)–C(31)	1.911(4)		
Re(1)–C(41)	1.911(4)		
Re(1)–C(51)	1.950(5)		
Re(1)–N(21)	2.175(3)		
Re(1)–N(11)	2.179(3)		
Re(1)–Cl(1)	2.4575(16)		
N(21)–Re(1)–N(11)	78.82(12)		
C(12)–N(1)–C(22)	123.7(3)		
C(12)–N(1)–C(61)	116.4(3)		
C(22)–N(1)–C(61)	115.3(3)		
Py1/py2 <sup>a</sup>	40.5		
substituent <sup>b</sup>	94.5		
<b>[Re(CO)<sub>3</sub>Cl(NAP)]</b>			
Re(1)–C(31)	1.901(4)	Re(2)–C(151)	1.909(4)
Re(1)–C(51)	1.913(4)	Re(2)–C(141)	1.910(4)
Re(1)–C(41)	1.918(4)	Re(2)–C(131)	1.911(4)
Re(1)–N(21)	2.178(3)	Re(2)–N(111)	2.193(3)
Re(1)–N(11)	2.180(3)	Re(2)–N(121)	2.200(3)
Re(1)–Cl(1)	2.4774(9)	Re(2)–Cl(2)	2.4701(9)
N(21)–Re(1)–N(11)	81.25(10)	N(111)–Re(2)–N(121)	80.83(11)
C(12)–N(1)–C(22)	124.7(3)	C(112)–N(2)–C(122)	114.3(3)
C(12)–N(1)–C(2)	116.3(3)	C(112)–N(2)–C(102)	120.3(3)
C(22)–N(1)–C(2)	116.4(3)	C(122)–N(2)–C(102)	122.7(3)
Py1/py2 <sup>a</sup>	35.5	Py1/py2 <sup>a</sup>	65.8
substituent <sup>b</sup>	90.0	substituent <sup>b</sup>	26.0

<sup>a</sup> Angle between the mean planes of the two coordinated pyridyl rings of the di(2-pyridyl)amine unit <sup>b</sup> Angle between the mean planes of the pendant substituent on the di(2-pyridyl)amine unit, and the mean plane defined by the amine N atom and the two pyridyl C2 atoms (e.g. for [Re(CO)<sub>3</sub>Cl(2-TPA)], the angle between the pendant pyridyl ring and the N(1)/C(12)/N(22) plane).

without any significant problems. For [Re(CO)<sub>3</sub>Cl(DP18C6)]·C<sub>4</sub>H<sub>8</sub>O and [Re(CO)<sub>3</sub>Cl(NMe)] a diffuse solvent correction was applied to eliminate areas of residual electron density which could not successfully be modelled as solvent molecules. In the structures of [Re(CO)<sub>3</sub>Cl(2-TPA)], [Re(CO)<sub>3</sub>Cl(3-TPA)],

[Re(CO)<sub>3</sub>Cl(NMe)] and [Re(CO)<sub>3</sub>Cl(NAP)] there are two crystallographically independent molecules in the asymmetric unit in each case.

### Optical spectroscopy

Samples of the investigated compounds were purified by column chromatography on alumina eluting with CH<sub>2</sub>Cl<sub>2</sub> or acetone/CH<sub>2</sub>Cl<sub>2</sub> before proceeding with optical studies, so to remove trace luminescent impurities. Absorption spectra of dilute dichloromethane solutions (2 × 10<sup>-5</sup> M) were obtained with a Perkin-Elmer Lambda 5 spectrophotometer. Luminescence spectra were obtained with a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Sample solutions were excited at the indicated wavelength, and dilution was adjusted to obtain absorbance values ≤ 0.15. While uncorrected luminescence band maxima are used throughout the text, corrected spectra were employed for the determination of the luminescence quantum yields. The correction procedure is based on use of a software which takes care of the wavelength dependent phototube response. From the area of the corrected luminescence spectra on an energy scale (cm<sup>-1</sup>), we obtained luminescence quantum yields  $\Phi$  for the samples with reference to [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> or quinine sulfate as standards ( $r$ ,  $\Phi_r$  = 0.028 in air-equilibrated water,<sup>20</sup> and 0.546 in 1 N H<sub>2</sub>SO<sub>4</sub>,<sup>21</sup> respectively), and by using eqn. (1):<sup>22</sup>

$$\frac{\Phi}{\Phi_r} = \frac{Abs_r n^2(area)}{Abs n_r^2(area)_r} \quad (1)$$

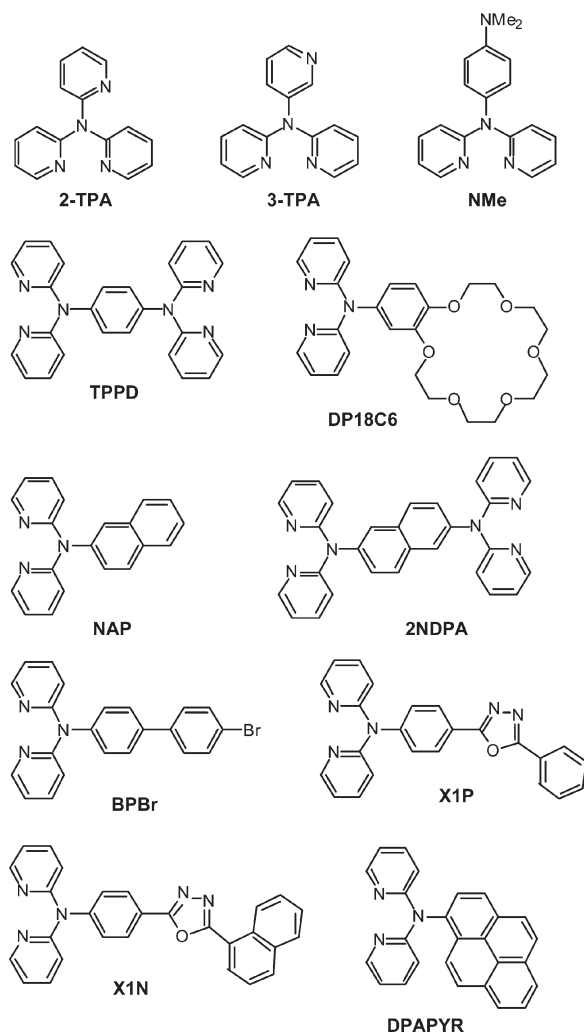
where  $Abs$  and  $n$  are absorbance value of the solution and the refractive index of the solvent, respectively. Band maxima and relative luminescence intensities were affected by an uncertainty of 2 nm and 20%, respectively. Luminescence lifetimes were obtained using an IBH single-photon counting spectrometer equipped with a nitrogen-filled thyratron gated lamp ( $\lambda_{exc}$  337 or 358 nm). The uncertainty in the lifetime values is within 8%.

## Results and discussion

### Syntheses of 2,2'-dipyridylamine derivatives and their rhenium(i) carbonyl chloride complexes

The new ligands (listed in Scheme 1) were prepared by the solid state reaction of 2,2'-dipyridylamine with the appropriate bromo-substituted aromatic derivative in the presence of base and a catalytic amount of Cu(II) following the routes described in the literature.<sup>9,10</sup> The use of K<sub>2</sub>CO<sub>3</sub> instead of KOH, and the efficient pre-mixing of reagents provided by method 2 (see Experimental section), gave better results than method 1. The same conclusion was reached by Pang and co-workers.<sup>10</sup> The 2,2'-dipyridylamine derivatives are insoluble in cold ethanol and usually could be easily separated from starting materials by recrystallization from ethanol; they were successfully characterised on the basis of their NMR and electron-impact mass spectra, as well as correct elemental analyses.

The new rhenium(i) carbonyl chloride complexes of some of these ligands were prepared in generally good (40–80%) yield by reacting Re(CO)<sub>5</sub>Cl with the appropriate ligand in toluene, followed by column chromatography on alumina. The low yield (14%) of [Re(CO)<sub>3</sub>Cl(3-TPA)] may, on the basis of mass spectral evidence, be due to the formation of the complex [Re(CO)<sub>3</sub>Cl( $\kappa^1$ -3-TPA)<sub>2</sub>] in which Re(i) is coordinated to two monodentate 3-TPA ligands, presumably through the nitrogen atoms of the 3-pyridine ring. This material however could not be isolated in pure form. All isolated Re(i) complexes gave correct elemental analyses and showed strong molecular ions in their FAB mass spectra (along with predictable fragmentation patterns due to loss of chloride and CO ligands). Three strong



Scheme 1 Ligands described in this paper.

carbonyl absorption bands were observed for rhenium(I) complexes in the IR region. Complexes were prepared with six of the ligands, as listed in the Experimental section, and the luminescence properties of these complexes are discussed below. The remaining ligands yielded Re complexes which were poorly soluble and could not be purified by crystallisation or chromatography to an extent sufficient for luminescence studies, so in these cases only the luminescence properties of the ligands are reported.

#### Structures of rhenium(I) carbonyl chloride complexes with 2,2'-dipyridylamine derivatives

The crystal structures of the five complexes  $[\text{Re}(\text{CO})_3\text{Cl}(\text{2-TPA})]$ ,  $[\text{Re}(\text{CO})_3\text{Cl}(\text{3-TPA})]$ ,  $[\text{Re}(\text{CO})_3\text{Cl}(\text{NMe})]$ ,  $[\text{Re}(\text{CO})_3\text{Cl}(\text{DP18C6})]$  and  $[\text{Re}(\text{CO})_3\text{Cl}(\text{NAP})]$  are shown in Figs. 1 to 5 respectively. In every case except  $[\text{Re}(\text{CO})_3\text{Cl}(\text{DP18C6})]$ , there are two crystallographically independent molecules in the asymmetric unit of which only one is shown. Selected bond distances and angles are in Table 2.

In all cases the dipyridylamine ligand is coordinated as a bidentate chelate *via* the two 2-pyridyl groups, giving a 6-membered chelate ring. The bond distances and angles around the pseudo-octahedral Re centres are similar between the complexes and unremarkable. In every case the central (tertiary amine) N atom of the dipyridylamine ligand is nearly planar, as shown by the fact that the sum of the three C–N–C angles is close to  $360^\circ$ . The angle between the mean planes of the coordinated pyridyl rings varies between *ca.*  $35^\circ$  and  $61^\circ$  across the series of complexes. The orientation of the third substituent

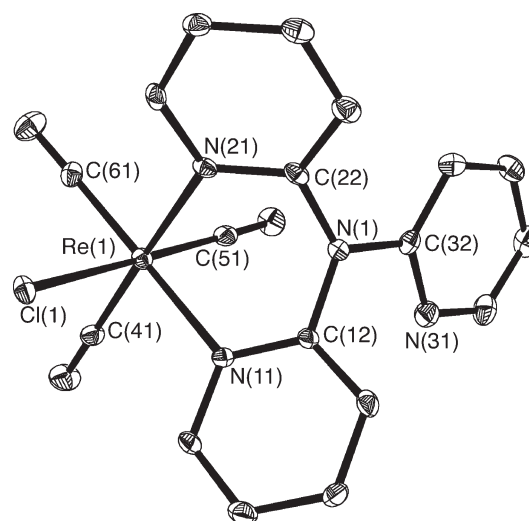


Fig. 1 Structure of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{2-TPA})]$  (only one of the two independent molecules is shown).

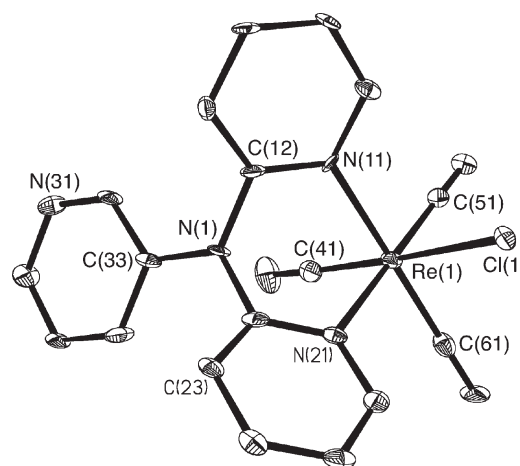


Fig. 2 Structure of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{3-TPA})]$  (only one of the two independent molecules is shown).

is even more variable; in one of the independent molecules in  $[\text{Re}(\text{CO})_3\text{Cl}(\text{3-TPA})]$  the pendant 3-pyridyl ring [atoms N(31) to C(36), Fig. 2] is almost coplanar with the plane of atoms N(1), C(12) and C(22), whereas in  $[\text{Re}(\text{CO})_3\text{Cl}(\text{NMe})]$  the corresponding angle, between the pendant phenyl ring and the C(12)/N(31)/C(22) plane is  $89.5^\circ$ . The variability of this parameter is particularly evident in the two crystallographically independent molecules of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{NAP})]$ , where in one case the naphthyl ring is exactly perpendicular to the adjacent  $\text{NC}_2$  plane but in the second case the angle is only  $26^\circ$ .

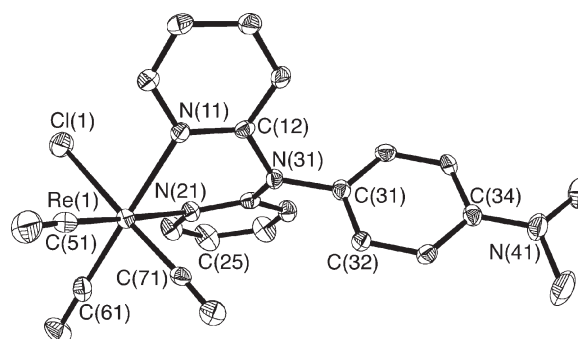


Fig. 3 Structure of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{NMe})]$  (only one of the two independent molecules is shown).

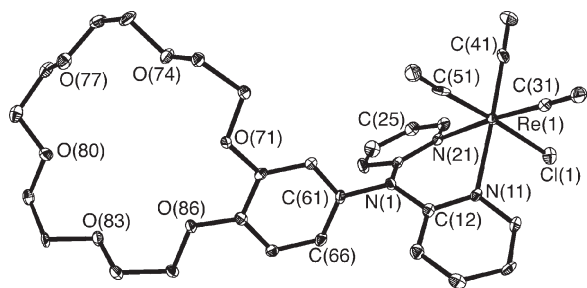


Fig. 4 Structure of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{DP18C6})]\cdot\text{thf}$  (solvent molecule not shown).

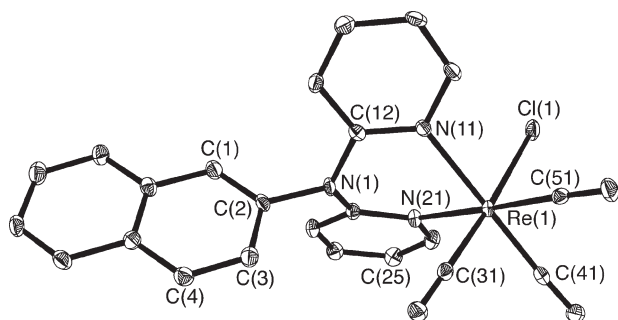


Fig. 5 Structure of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{NAP})]$  (only one of the two independent molecules is shown).

### Optical spectroscopy

In Table 3 are collected relevant absorption features, luminescence band maxima, and luminescence quantum yields and lifetimes for the investigated 2,2'-dipyridylamine derivatives. Fig. 6 displays absorption and luminescence spectra for six of these compounds. Data for the Re(i) complexes of the latter group of ligands is collected in Table 4. All results were obtained at room temperature in air-equilibrated dichloromethane. For the luminescence studies  $\lambda_{\text{exc}}$  was 330 nm (steady state spectra) or 337 nm (lifetimes); no dependence on excitation wavelength was observed. Within Tables 3 and 4, we have arbitrarily listed the compounds by sorting out an increasing value for the emission wavelength,  $\lambda_{\text{em}}$ .

The ligand absorption profiles illustrated in Fig. 6 (and described in Table 3) are characterized by two band maxima (or one maximum and a shoulder) in the 270–370 nm portion of the UV region. The lowest-energy band around 300–310

Table 3 Spectroscopic and photophysical parameters for the investigated ligands<sup>a</sup>

	Absorption $\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )	Emission <sup>b</sup>		
		$\lambda_{\text{em}}/\text{nm}$	$\Phi$	$\tau/\text{ns}$
2-TPA	269 (14 700), 297 (19 450)	374	0.08	3.6
NAP	273 (25 900), 307 (20 800)	386	0.22	1.7
BPBr	275 (sh), 309 (27 700)	390	0.23	1.0
X1P	343 (30 300)	399	0.69	1.5
2NDPA	315 (37 750)	405	0.22	4.3
DPAPYR	354 (21 000)	415	0.74	3.9
X1N	349 (34 750)	421	0.73	2.1
DP18C6	279 (15 000), 293 (15 100)	438	0.10	5.3
TPPD	280 (sh), 306 (33 400)	452	0.06	2.5
NMe	279 (21 200), 311 (sh)	512	0.01	0.9

<sup>a</sup> At room temperature, in dichloromethane solvent. <sup>b</sup> Excitation performed at  $\lambda = 330$  nm for steady-state spectra, and at 337 nm for lifetime measurements.

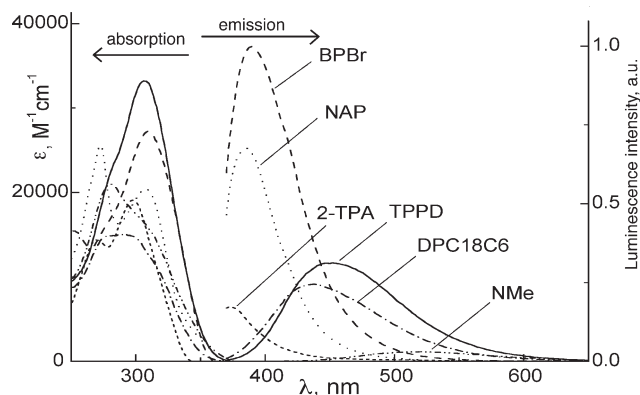


Fig. 6 Ground state absorption and luminescence spectra of the indicated ligands in dichloromethane ( $\lambda_{\text{exc}} = 330$  nm for the luminescence spectra).

nm is probably due to (predominant) amine N-to ring CT transitions, as expected for aromatic amines.<sup>12</sup> Higher-lying features in the 250–270 nm region are ascribable to pyridine-based (LC) transitions. In some cases, the distinct profile for an aryl residue is easily identified. For instance, the typical well resolved pyrene-based absorption (250–300 nm)<sup>23</sup> is found in the spectrum of DPAPYR (not shown in Fig. 6).

The luminescence band maximum for the ligands is found to vary from 374 to 512 nm, Table 3, which represents an interesting outcome having in mind the possible utilisation of these compounds in the OLED technology.<sup>9,10</sup> The luminescence profiles are broad and this might be traced back to the CT character for the emitting level. The ligands exhibit good luminescence intensities and lifetimes on the nanosecond time scale, as expected for this type of amines.<sup>9–12</sup> The luminescence quantum yield,  $\Phi$ , is however a changeable figure in the series, see Table 3. On one extreme, very high values for  $\Phi$  (not far from unity), are found for X1P, DPAPYR, and X1N. On the contrary, for NMe, the luminescence intensity is the poorest in the series. This may be due to a combination of at least two factors: the presence of an aliphatic amine centre and the energy gap law for radiationless transitions. For the former issue, it is known that the aliphatic amine centres may act as electron donors,<sup>23</sup> provided some energetic requirements are met, thus causing luminescence quenching of the interacting excited unit. For the latter issue, one may notice that for NMe the detected luminescent level is the lowest in energy within the studied series. This is precisely the condition for enhanced radiationless rate constants in accord with the “energy gap law”.<sup>24</sup>

Absorption and luminescence properties of the Re(i) complexes of some of the dipyrilidylamines studied are summarized in Table 4; only those complexes that were sufficiently soluble

Table 4 Spectroscopic and photophysical parameters for the investigated Re(i) complexes.<sup>a</sup>

Complex	Absorption $\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )	Emission <sup>b</sup>		
		$\lambda_{\text{em}}/\text{nm}$	$\Phi$	$\tau/\text{ns}^c$
$[\text{Re}(\text{CO})_3\text{Cl}(\text{NAP})]$	255 (sh), 293 (18 900)	—	—	—
$[\text{Re}(\text{CO})_3\text{Cl}(\text{BPBr})]$	263 (32 500), 295 (sh)	—	—	—
$[\text{Re}(\text{CO})_3\text{Cl}(\text{DP18C6})]$	251 (19 600), 295 (17 400)	—	—	—
$[\text{Re}(\text{CO})_3\text{Cl}(\text{2-TPA})]$	266 (13 900), 307 (16 000)	492	$<10^{-5}$	nd
$[\text{Re}(\text{CO})_3\text{Cl}(\text{TPPD})]$	259 (22 000), 304 (22 600)	516	0.04	42
$[\text{Re}(\text{CO})_3\text{Cl}(\text{NMe})]$	263 (30 000), 296 (21 000)	582	$<10^{-5}$	nd

<sup>a</sup> At room temperature, in dichloromethane solvent. <sup>b</sup> Excitation performed at  $\lambda = 330$  nm for steady-state spectra, and at 337 nm for lifetime measurements. <sup>c</sup> nd = not detected.



to be re-purified by chromatography and recrystallisation were analysed. In general terms, the intense absorption bands in the UV region should be associated with LC and CT transitions centred on the corresponding dipyriddyamine unit. These bands are likely to obscure the much weaker MLCT features, which appear as an additional tail towards the visible region.<sup>13–15</sup> For illustration purposes, in Fig. 7 are compared the absorption spectra for **TPPD** and  $[\text{Re}(\text{CO})_3\text{Cl}(\text{TPPD})]$ . Regarding the luminescence properties of the Re(I) complexes, we notice that  $[\text{Re}(\text{CO})_3\text{Cl}(\text{TPPD})]$  is the only one showing a moderate luminescence intensity, Fig. 7 and Table 4. Its luminescence quantum yield, band maximum, lifetime, and the broad luminescence profile are all consistent with a Re-to-L CT nature for the emission.<sup>13–15</sup> The other complexes show essentially no (or very weak) luminescence apart from what can obviously be ascribed to very small (<0.1%) traces of the luminescent free ligand. At any rate, for all cases but one, the Re(I) complexes are practically not luminescent, in contrast to the strong luminescence intensity of the incorporated dipyriddyamine ligand. In order to discuss possible reasons for this behavior, we notice that (i) the Re → L CT lowest-lying level is always expected to be lower in energy than the (formerly luminescent) level centred on the coordinated amine unit (see Tables 3 and 4), and that (ii) coordination of the ligand at the Re(I) centre takes place with formation of a 6-membered chelate ring (see above), as opposed to a 5-membered one for most luminescent Re(I)-polypyridine complexes.<sup>13–15</sup> This is likely to result in a lower ligand field strength for the present cases. As a consequence, lower-lying, thermally accessible d–d MC levels could provide an efficient non-radiative path for disposal of the excitation energy in the Re(I) complexes reported here. This behaviour is well known for derivatives of  $[\text{Ru}(\text{bipy})_3]^{2+}$  in which the ligand field strength around the metal is reduced by steric distortions,<sup>25</sup> and has recently been demonstrated for a range of Re(I)-tricarbonyl-diimine complexes,<sup>26</sup> although it should be noted that a range of other non-radiative decay pathways are in principle available.<sup>15c,26</sup>

## Conclusion

In conclusion, we have prepared a new series of ligands based on the dpa core, which show moderate to strong luminescence. Several of their complexes with  $\{\text{Re}(\text{CO})_3\text{Cl}\}$  units have been prepared and structurally characterised; with one exception these are non-luminescent, the exception from  $[\text{Re}(\text{CO})_3\text{Cl}(\text{tpdp})]$  in which one di(2-pyridyl)amine site is occupied by a  $\{\text{Re}(\text{CO})_3\text{Cl}\}$  unit but the other is vacant.

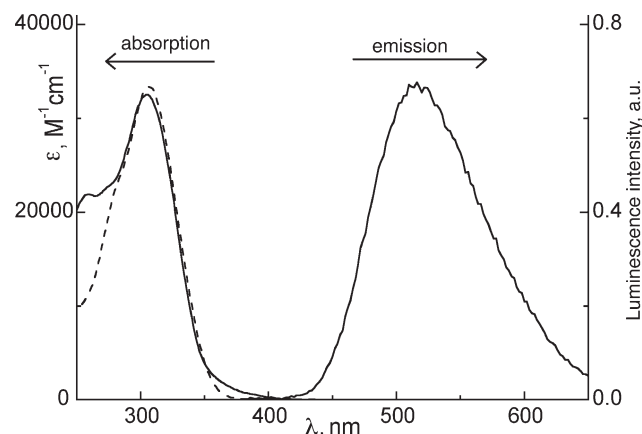


Fig. 7 Ground state absorption spectrum and luminescence spectrum ( $\lambda_{\text{exc}} = 330 \text{ nm}$ ) of  $[\text{Re}(\text{CO})_3\text{Cl}(\text{TPPD})]$  (full line); the absorption spectrum of **TPPD** is also shown (dashed line); solvent was dichloromethane.

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## References

- (a) L. P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1990, 3835; (b) G. J. Pyrka, M. Elmekki and A. A. Pinkerton, *J. Chem. Soc., Chem. Commun.*, 1991, 84; (c) S. Aduldech and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1991, 993; (d) J. T. Sheu, C. S. Lin, I. Chao, C. C. Wang and S. M. Peng, *Chem. Commun.*, 1996, 315; (e) X. M. Wang, H. S. Sun and X. Z. You, *Polyhedron*, 1996, **15**, 3543; (f) F. Uguzzoli, A. M. M. Lanfredi, N. Marsich and A. Camus, *Inorg. Chim. Acta*, 1997, **256**, 1; (g) H. Gornitzka and D. Stalke, *Eur. J. Inorg. Chem.*, 1998, 311; (h) F. A. Cotton, L. M. Daniels, G. T. Jordan IV and C. A. Murillo, *Polyhedron*, 1998, **17**, 589; (i) J. Y. Lu, T. J. Schroeder, A. M. Babb and M. Olmstead, *Polyhedron*, 2001, **20**, 2445; (j) M. Du, Y. M. Guo, C. S. Chen, X. H. Bu and J. Ribas, *Inorg. Chim. Acta*, 2003, **346**, 207 and references cited therein; (k) T. B. Tsao, G. H. Lee, C. Y. Yeh and S. M. Peng, *Dalton Trans.*, 2003, 1465; (l) J. F. Berry, F. A. Cotton, P. Lei and C. A. Murillo, *Inorg. Chem.*, 2003, **42**, 377; (m) J. A. Cabeza, I. del Rio, S. Garcia-Granda, V. Riera and M. Suarez, *Organometallics*, 2002, **21**, 2540.
- (a) K. Y. Ho, W. Y. Yu, K. K. Cheung and C. M. Che, *Chem. Commun.*, 1998, 2101; (b) K. Y. Ho, W. Y. Yu, K. K. Cheung and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1999, 1581.
- H. G. Zhu, M. Strobele, Z. Yu, Z. Wang, H. J. Meyer and X. Z. You, *Inorg. Chem. Commun.*, 2001, **4**, 577.
- J. Ashenhurst, L. Brancalion, S. Gao, W. Liu, H. Schmider, S. Wang, G. Wu and Q. G. Wu, *Organometallics*, 1998, **17**, 5334.
- (a) W. L. Huang, D. P. Segers and M. K. DeArmond, *J. Phys. Chem.*, 1981, **85**, 2080; (b) J. R. Lee, Y. R. Liou and W. L. Huang, *Inorg. Chim. Acta*, 2001, **319**, 83.
- (a) D. P. Segers and M. K. DeArmond, *J. Phys. Chem.*, 1982, **86**, 3768; (b) R. L. Blakley, M. L. Myrick and M. K. DeArmond, *J. Am. Chem. Soc.*, 1986, **108**, 7843; (c) R. L. Blakley and M. K. DeArmond, *J. Am. Chem. Soc.*, 1987, **109**, 4895; (d) M. R. McDevitt, Y. Ru and A. W. Addison, *Trans. Met. Chem.*, 1993, **18**, 197; (e) N. Nagao, M. Mukaida, E. Miki, K. Mizumachi and T. Ishimori, *Bull. Chem. Soc. Japan*, 1994, **67**, 2447.
- M. Bakir and J. A. M. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1997, 3571.
- (a) K. K. Mosny and R. H. Crabtree, *Inorg. Chim. Acta*, 1996, **247**, 93; (b) L. F. Szczepura, L. M. Witham and K. J. Takeuchi, *Coord. Chem. Rev.*, 1998, **174**, 5; (c) T. Schareina, G. Hillebrand, H. Fuhrmann and R. Kempe, *Eur. J. Inorg. Chem.*, 2001, 2421; (d) S. P. Foxon, O. Walter and S. Schindler, *Eur. J. Inorg. Chem.*, 2002, 111; (e) P. Gamez, P. de Hoog, O. Roubeau, M. Lutz, W. L. Driessen, A. L. Spek and J. Reedijk, *Chem. Commun.*, 2002, 1488; (f) P. de Hoog, P. Gamez, W. L. Driessen and J. Reedijk, *Tetrahedron Lett.*, 2002, 6783; (g) P. de Hoog, P. Gamez, O. Roubeau, M. Lutz, W. L. Driessen, A. L. Spek and J. Reedijk, *New J. Chem.*, 2003, **27**, 18; (h) P. Gamez, P. de Hoog, M. Lutz, W. L. Driessen, A. L. Spek and J. Reedijk, *Polyhedron*, 2003, **22**, 205.
- (a) W. Y. Yang, H. Schmider, Q. G. Wu, Y. S. Zhang and S. N. Wang, *Inorg. Chem.*, 2000, **39**, 2397; (b) W. Y. Yang, L. Chen and S. N. Wang, *Inorg. Chem.*, 2001, **40**, 507; (c) C. Seward, J. Pang and S. Wang, *Eur. J. Inorg. Chem.*, 2002, 1390; (d) Y. J. Kang and S. N. Wang, *Tetrahedron Lett.*, 2002, **43**, 3711; (e) W. L. Jia, D. Song and S. Wang, *J. Org. Chem.*, 2003, **68**, 701; (f) W. L. Jia, Q. D. Liu, D. T. Song and S. I. Wang, *Organometallics*, 2003, **22**, 321; (g) C. Seward, J. L. Chan, D. T. Song and S. N. Wang, *Inorg. Chem.*, 2003, **42**, 1112; (h) Y. J. Kang, C. Seward, D. T. Song and S. N. Wang, *Inorg. Chem.*, 2003, **42**, 2789.
- J. Pang, Y. Tao, S. Freiberg, X. P. Yang, M. D'Orio and S. N. Wang, *J. Mater. Chem.*, 2002, **12**, 206.
- J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown and S. N. Wang, *Angew. Chem. Int. Ed.*, 2001, **40**, 4042.
- T. Ganguly, S. K. Sarkar, A. Mitra and P. K. Mallick, *J. Photochem. Photobiol. A: Chem.*, 1996, **94**, 113.
- (a) R. V. Slone, K. D. Benkstein, S. Belanger, J. T. Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, **171**, 221; (b) D. J. Stufkens and A. Vlcek, *Coord. Chem. Rev.*, 1998, **177**, 127; (c) A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 2000, **200–202**, 991; (d) M. D. Ward and F. Barigelletti, *Coord. Chem. Rev.*, 2001, **216–217**, 127; (e) S. S. Sun and A. J. Lees, *Coord. Chem. Rev.*, 2002, **230**, 171.

- 14 (a) D. A. Bardwell, F. Barigelletti, R. L. Cleary, L. Flamigni, M. Guardigli, J. C. Jeffery and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 2438; (b) S. Encinas, K. L. Bushell, S. M. Couchman, J. C. Jeffery, M. D. Ward, L. Flamigni and F. Barigelletti, *J. Chem. Soc., Dalton Trans.*, 2000, 1783; (c) N. M. Shavaleev, G. Accorsi, Z. R. Bell and M. D. Ward, *Inorg. Chim. Acta*, 2003, **351**, 159.
- 15 (a) P. J. Giordano, S. M. Fredericks, M. S. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1978, **100**, 2257; (b) R. Lin and T. F. Guarr, *Inorg. Chim. Acta*, 1990, **167**, 149; (c) L. A. Worl, R. Duesing, P. Chen, L. D. Ciana and T. J. Meyer, *J. Chem. Soc., Dalton Trans.*, 1991, 849; (d) F. W. M. Vanhelfmont, M. V. Rajasekharan, H. U. Gudel, S. C. Capelli, J. Hauser and H. B. Burgi, *J. Chem. Soc., Dalton Trans.*, 1998, 2893; (e) W. M. Xue, N. Goswami, D. M. Eichhorn, P. L. Orizondo and D. P. Rillema, *Inorg. Chem.*, 2000, **39**, 4460; (f) D. R. Striplin and G. A. Crosby, *Coord. Chem. Rev.*, 2001, **211**, 163; (g) K. A. Walters, K. D. Ley, C. S. P. Cavalaheiro, S. E. Miller, D. Gosztola, M. R. Wasielewski, A. P. Bussandri, H. van Willigen and K. S. Schanze, *J. Am. Chem. Soc.*, 2001, **123**, 8329; (h) X. Y. Chen, F. J. Femia, J. W. Babich and J. Zubietta, *Inorg. Chim. Acta*, 2001, **315**, 66; (i) B. Manimaran, T. Rajendran, Y. L. Lu, G. H. Lee, S. M. Peng and K. L. Lu, *J. Chem. Soc., Dalton Trans.*, 2001, 515; (j) N. Armaroli, G. Accorsi, D. Felder and J. F. Nierengarten, *Chem. Eur. J.*, 2002, **8**, 2314; (k) R. Czerwieniec, A. Kapturkiewicz, R. Anulewicz-Ostrowska and J. Nowacki, *J. Chem. Soc., Dalton Trans.*, 2002, 3434; (l) A. Del Guerso, S. Leroy, F. Fages and R. H. Schmehl, *Inorg. Chem.*, 2002, **41**, 359; (m) J. L. Zuo, W. F. Fu, C. M. Che and K. K. Cheung, *Eur. J. Inorg. Chem.*, 2003, 255; (n) V. W. W. Yam, K. M. C. Wong, S. H. F. Chong, V. C. Y. Lau, S. C. F. Lam, L. J. Zhang and K. K. Cheung, *J. Organomet. Chem.*, 2003, **670**, 205.
- 16 (a) K. A. Kneas, W. Xu, J. N. Demas, B. A. DeGraff and A. P. Zipp, *J. Fluoresc.*, 1998, **8**, 295; (b) I. Costa, M. Montalti, P. Pallavicini, A. Perotti, L. Prodi and N. Zaccheroni, *J. Organomet. Chem.*, 2000, **593–594**, 267; (c) K. K. W. Lo, D. C. M. Ng, W. K. Hui and K. K. Cheung, *J. Chem. Soc., Dalton Trans.*, 2001, 2634.
- 17 (a) X. Gong, P. K. Ng and W. K. Chan, *Adv. Mater.*, 1998, **10**, 1337; (b) W. K. Chan, P. K. Ng, X. Gong and S. J. Hou, *Appl. Phys. Lett.*, 1999, **75**, 3920; (c) Y. Li, Y. Wang, Y. Zhang, Y. Wu and J. Shen, *Synth. Met.*, 1999, **99**, 257; (d) P. K. Ng, X. Gong, S. H. Chan, L. S. M. Lam and W. K. Chan, *Chem. Eur. J.*, 2001, **7**, 4358; (e) K. Wang, L. Huang, L. Gao, L. Jin and C. Huang, *Inorg. Chem.*, 2002, **41**, 3353; (f) S. Ranjan, S. Y. Lin, K. C. Hwang, Y. Chi, W. L. Ching, C. S. Liu, Y. T. Tao, C. H. Chien, S. M. Peng and G. H. Lee, *Inorg. Chem.*, 2003, **42**, 1248.
- 18 G. M. Sheldrick: SADABS, A program for absorption correction with the Siemens SMART area-detector system; University of Göttingen, 1996.
- 19 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
- 20 K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2967.
- 21 S. R. Meech and D. Phillips, *J. Photochem.*, 1983, **23**, 193.
- 22 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
- 23 S. L. Murov, I. Carmichael, G. L. Hug, *Handbook of Photochemistry*, M. Dekker, New York, 1993.
- 24 R. Englman and J. Jortner, *Mol. Phys.*, 1970, **18**, 145.
- 25 (a) R. H. Fabian, D. M. Klassen and R. W. Sonntag, *Inorg. Chem.*, 1980, **19**, 1977; (b) J. M. Kelly, C. Long, C. M. O'Connell, J. G. Vos and A. H. A. Tinnemenans, *Inorg. Chem.*, 1983, **22**, 2818; (c) E. C. Constable, M. J. Hannon, A. M. W. Cargill Thompson, D. A. Tocher and J. V. Walker, *Supramol. Chem.*, 1993, **2**, 243; (d) A. M. Barthram, M. D. Ward, A. Gessi, N. Armaroli, L. Flamigni and F. Barigelletti, *New J. Chem.*, 1998, **22**, 913.
- 26 K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I. P. Clark, M. W. George, F. P. A. Johnson and J. J. Turner, *J. Am. Chem. Soc.*, 2002, **124**, 11488.