Stretching the phenazine MO in dppz: The effect of phenyl and phenyl-ethynyl groups on the photophysics of Re(I) dppz complexes†

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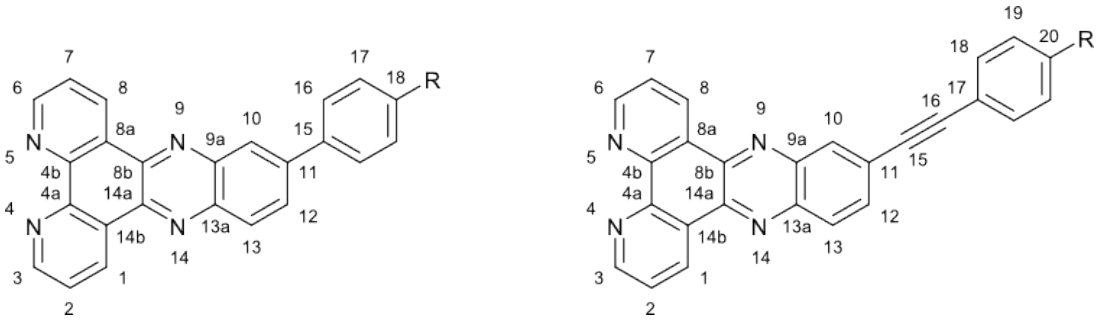

Fig. 1 Numbering scheme used for NMR assignments.

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NMR data

11-(4-*tert*-butylphenyl)dipyrido[3,2-a:2',3'-c]phenazine (1a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.54 (2H, m, $H_{1,8}$), 9.25 (2H, m, $H_{3,6}$), 8.45 (1H, d, J = 1.5 Hz, H_{10}), 8.30 (1H, d, J = 8.8 Hz, H_{13}), 8.17 (1H, dd, J = 8.8, 2.1 Hz, H_{12}), 7.80 (2H, d, J = 8.7 Hz, H_{16}), 7.75 (2H, m, $H_{2,7}$), 7.60 (2H, d, J = 8.7 Hz, H_{17}), 1.42 (9H, s, ^{t}Bu) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.48($C_{3/6}$), 152.37($C_{3/6}$), 151.98 (C_{18}), 148.10 ($C_{4a/4b}$), 147.98 ($C_{4a/4b}$), 143.27 (C_{11}), 142.84 (C_{9a}), 141.89 (C_{13a}), 141.35 ($C_{8b/14a}$), 140.66 ($C_{8b/14a}$), 136.55 (C_{15}), 133.98 ($C_{1/8}$), 133.93 ($C_{1/8}$), 130.71 (C_{12}), 129.84 (C_{13}), 127.77 ($C_{8a/14b}$), 127.69 ($C_{8a/14b}$), 127.39 (C_{16}), 126.33 (C_{17}), 126.19 (C_{10}), 124.29 ($C_{2/7}$), 124.28 ($C_{2/7}$), 34.88 (^{t}Bu), 31.49 (^{t}Bu) ppm.

11-(4-cyanophenyl)dipyrido[3,2-a:2',3'-c]phenazine (2a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (2H, m, $H_{1,8}$), 9.31 (2H, m, $H_{3,6}$), 8.58 (1H, d, J = 2.2 Hz, H_{10}), 8.46 (1H, d, J = 8.8 Hz, H_{13}), 8.17 (1H, dd, J = 8.9, 2.1 Hz, H_{12}), 7.97 (2H, d, J = 8.7 Hz, H_{16}), 7.87 (2H, d, J = 8.6 Hz, H_{17}), 7.83 (2H, m, $H_{2,7}$) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.64 ($C_{3/6}$), 152.60 ($C_{3/6}$), 147.67 ($C_{4a,4b}$), 144.03 (C_{15}), 142.66 (C_{9a}), 142.44 (C_{13a}), 141.82 ($C_{8b,14a}$), 141.49 (C_{11}), 134.62 ($C_{1/8}$), 134.52 ($C_{1/8}$), 133.13 (C_{17}), 130.65 (C_{13}), 130.17 (C_{12}), 128.42 (C_{16}), 127.84 (C_{10}), 127.77 ($C_{8a,14b}$), 124.69 ($C_{2,7}$), 118.72 (CN), 112.43 (C_{18}) ppm.

11-((4-*tert*-butylphenyl)ethynyl)dipyrido[3,2-a:2',3'-c]phenazine (1b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (2H, m, $H_{1,8}$), 9.27 (2H, m, $H_{3,6}$), 8.49 (1H, d, J = 1.7 Hz, H_{10}), 8.28 (1H, d, J = 8.8 Hz, H_{13}), 7.98 (1H, dd, J = 8.8, 1.8 Hz, H_{12}), 7.79 (2H, m, $H_{2,7}$), 7.58 (2H, d, J = 8.6 Hz, H_{18}), 7.45 (2H, d, J = 8.6 Hz, H_{19}), 1.36 (9H, s, ^{t}Bu) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.86 ($C_{3/6}$), 152.80 ($C_{3/6}$), 152.60 (C_{20}), 148.64 ($C_{4a/4b}$), 148.61 ($C_{4a/4b}$), 142.42 (C_{9a}), 142.19 (C_{13a}), 141.89 ($C_{8b/14a}$), 141.25 ($C_{8b/14a}$), 133.97 ($C_{1/8}$), 133.93 ($C_{1/8}$), 133.59 (C_{12}), 132.28 (C_{10}), 131.78 (C_{18}), 129.63 (C_{13}), 127.65 ($C_{8a/14b}$) 127.63 ($C_{8a/14b}$), 126.28 (C_{11}), 125.71 (C_{19}), 124.35 ($C_{2/7}$), 124.33 ($C_{2/7}$), 119.72 (C_{17}), 93.82 (C_{16}), 88.40 (C_{15}), 35.09 (^{t}Bu), 31.33 (^{t}Bu) ppm.

11-((4-cyanophenyl)ethynyl)dipyrido[3,2-a:2',3'-c]phenazine (2b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (2H, m, $H_{1,8}$), 9.29 (2H, m, $H_{3,6}$), 8.53 (1H, s, H_{10}), 8.32 (1H, d, J = 8.7 Hz, H_{13}), 7.98 (1H, d, J = 8.6 Hz, H_{12}), 7.81 (2H, m, $H_{2,7}$), 7.72 (4H, m, $H_{18,19}$) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.79 ($C_{3,6}$), 148.07 ($C_{4a,4b}$), 142.48 (C_{13a}), 142.20 (C_{9a}), 141.94 ($C_{8b/14a}$), 141.55 ($C_{8b/14a}$), 134.36 ($C_{1/8}$), 134.31 ($C_{1/8}$), 133.21 (C_{12}), 133.16 (C_{10}), 132.49 ($C_{18/19}$), 132.37 ($C_{18/19}$), 130.01 (C_{13}), 127.62 ($C_{8a,14b}$), 127.59 (C_{17}), 124.89 (C_{11}), 124.56 ($C_{2,7}$), 118.47 (C_{20}), 112.44 (CN), 92.82 (C_{15}), 91.38 (C_{16}) ppm.

***fac*-Chlorotricarbonyl(11-(4-*tert*-butylphenyl)dipyrido[3,2-a:2',3'-c]phenazine)rhenium(I).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (2H, m, $H_{1,8}$), 9.46 (2H, m, $H_{3,6}$), 8.61 (1H, d, J = 1.9 Hz, H_{10}), 8.47 (1H, d, J = 8.9 Hz, H_{13}), 8.35 (1H, dd, J = 8.9, 2.0 Hz, H_{12}), 8.02 (2H, m, $H_{2,7}$), 7.84 (2H, d, J = 8.4 Hz, H_{16}), 7.63 (2H, d, J = 8.4 Hz, H_{17}), 1.43 (9H, s, ^{t}Bu) ppm.

***fac*-Chlorotricarbonyl(11-(4-cyanophenyl)dipyrido[3,2-a:2',3'-c]phenazine)rhenium(I).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (2H, m, $H_{1,8}$), 9.49 (2H, d, J = 5.3 Hz, $H_{3,6}$), 8.67 (1H, d, J = 2.0 Hz, H_{10}), 8.57 (1H, d, J = 8.9 Hz, H_{13}), 8.30 (1H, dd, J = 9.0 Hz, 2.1 Hz, H_{12}), 8.05 (2H, m, $H_{2,7}$), 7.99 (2H, d, J = 8.4 Hz, H_{16}), 7.90 (2H, d, J = 8.3 Hz, H_{17}) ppm.

***fac*-Chlorotricarbonyl(11-((4-*tert*-butylphenyl)ethynyl)dipyrido[3,2-a:2',3'-c]phenazine)rhenium(I).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (2H, m, $H_{1,8}$), 9.47 (2H, m, $H_{3,6}$), 8.54 (1H, d, J = 1.8 Hz, H_{10}), 8.35 (1H, d, J = 8.8 Hz, H_{13}), 8.10 (1H, dd, J = 7.5, 2.2 Hz, H_{12}), 8.03 (2H, m, $H_{2,7}$), 7.60 (2H, d, J = 8.3 Hz, H_{18}), 7.47 (2H, d, J = 8.4 Hz, H_{19}), 1.37 (9H, s, ^{t}Bu) ppm.

***fac*-Chlorotricarbonyl(11-((4-cyanophenyl)ethynyl)dipyrido[3,2-a:2',3'-c]phenazine)rhenium(I).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (2H, m, $H_{1,8}$), 9.69 (2H, m, $H_{3,6}$), 8.65 (1H, d, J = 1.6 Hz, H_{10}), 8.46 (1H, d, J = 9.0 Hz, H_{13}), 8.14 (1H, dd, J = 8.9, 1.3 Hz, H_{12}), 8.13 (2H, m, $H_{2,7}$), 7.74 (4H, m, $H_{18,19}$) ppm.

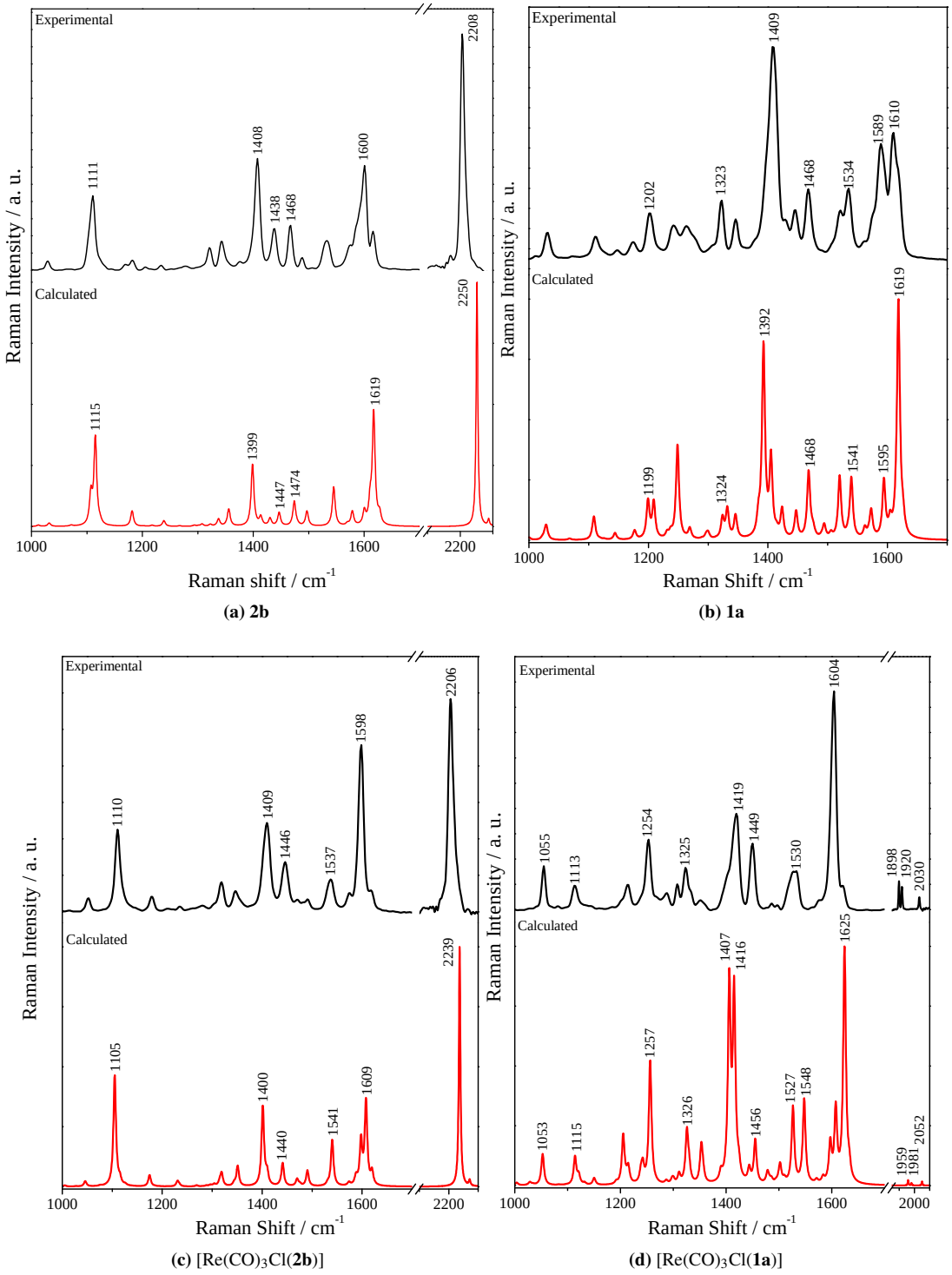
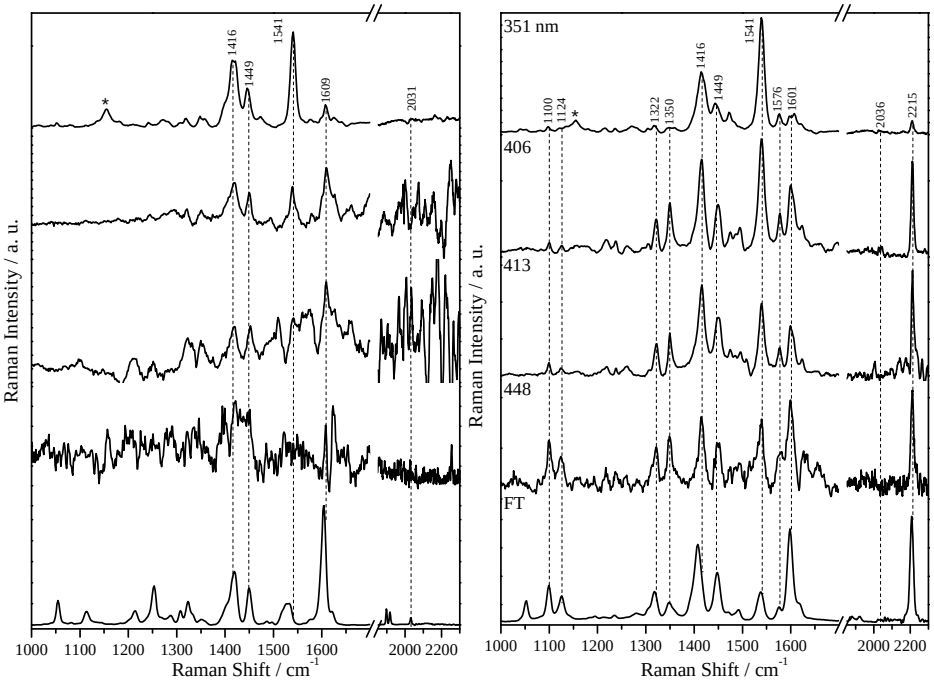
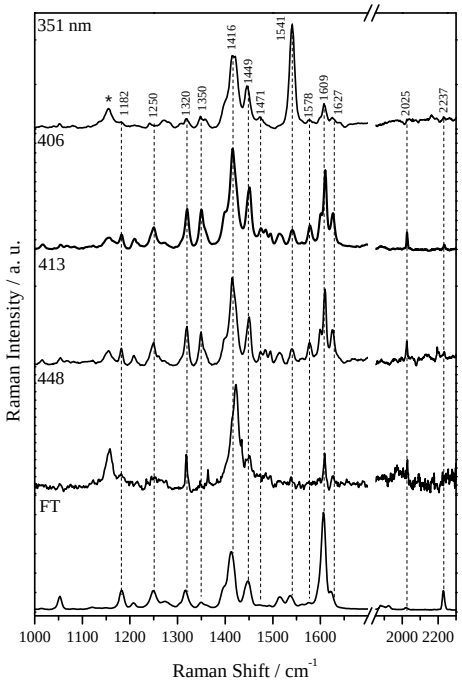


Fig. 2 Experimental FT-Raman and DFT calculated Raman spectra of selected compounds.

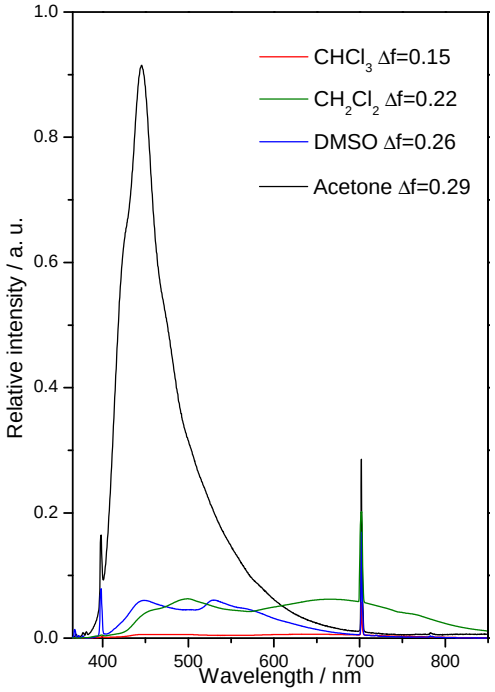


(a) [$Re(CO)_3Cl$(**1a**)] **(b)** [$Re(CO)_3Cl$(**1b**)]

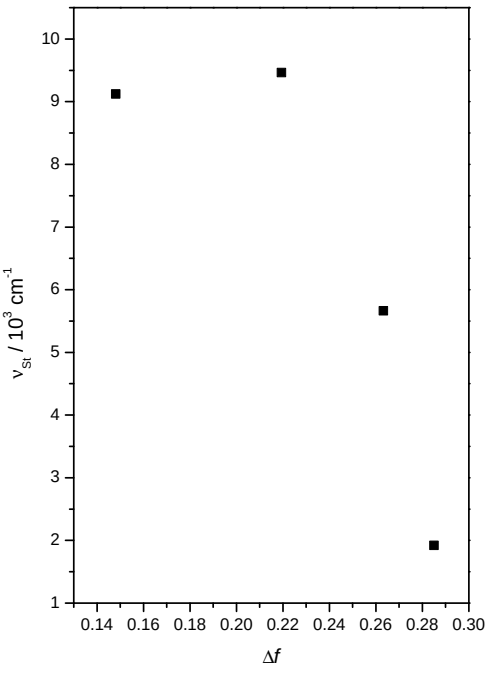


(c) [$Re(CO)_3Cl$(**2a**)]

Fig. 3 Resonance Raman spectra of complexes in CH_2Cl_2 solution.

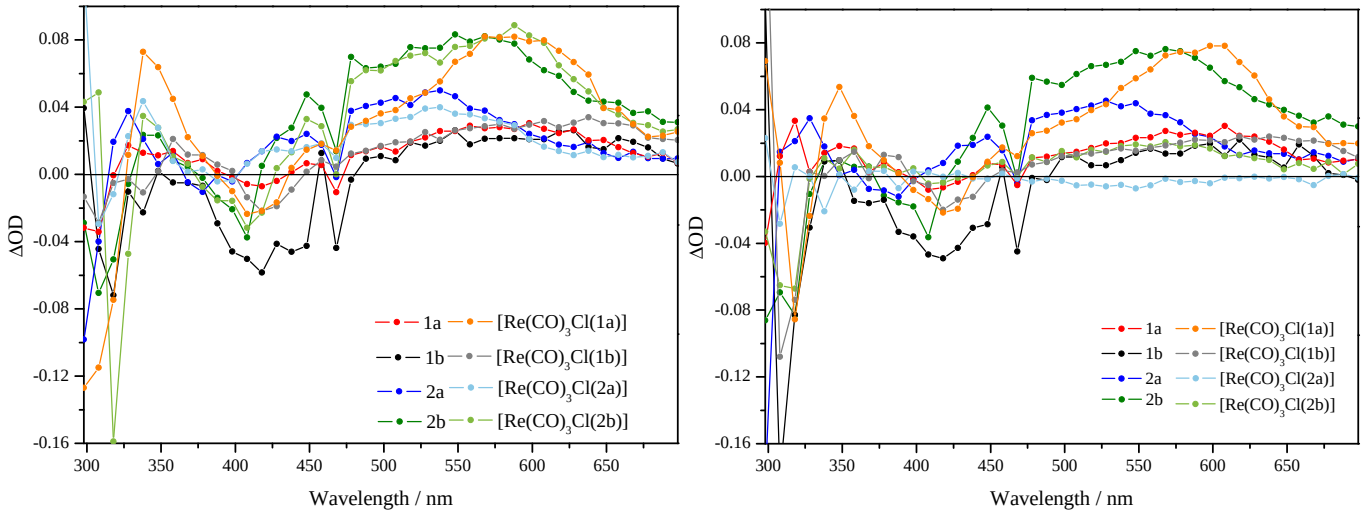


(a) Variable solvent emission spectra of [Re(CO)$_3$Cl(**2b**)]



(b) Plot of Stokes shift vs Δ*f* for [Re(CO)$_3$Cl(**2b**)] showing two different gradients.

Fig. 4 Emission spectra in various solvents for [Re(CO)$_3$Cl(**2b**)] and plot of Stokes shift vs Δ*f*, showing why the Lippert-Mataga equation cannot be applied to this data.



(a) **(b)**

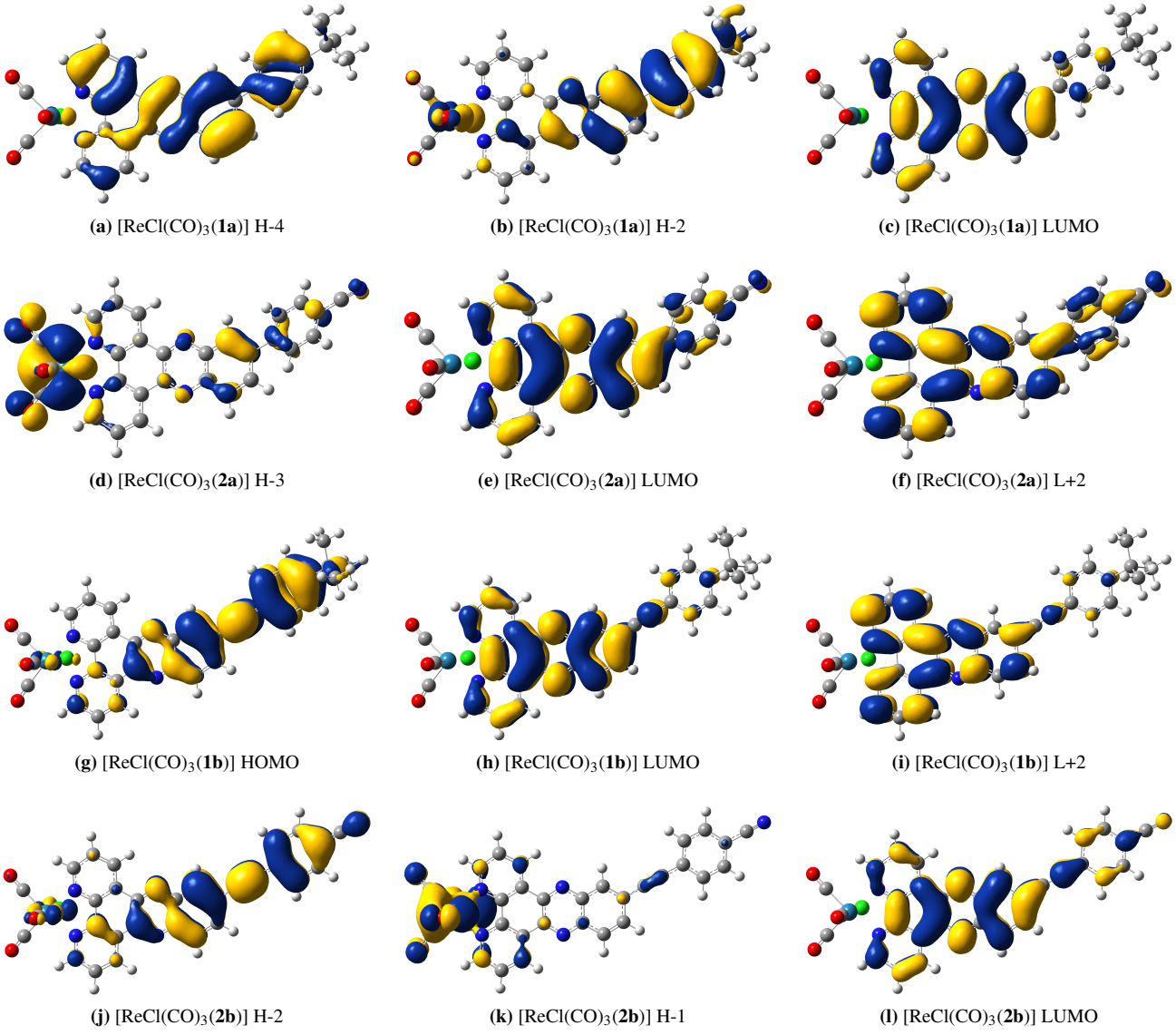
Fig. 5 Transient absorption spectra obtained at (a) 40 ns and (b) 200 ns after 355 nm excitation. Compounds are in deoxygenated DCM solution with concentration of approximately 1×10^{-5} M.

Table 1 Electronic absorption and TD-DFT calculated (dichloromethane solvent field implemented with scrf model) data.

Compound	λ (ε) / nm (10^{-4} $M^{-1}cm^{-1}$)	B3LYP (*f*) / nm	MO configuration (%)	CAM B3LYP (*f*) / nm	MO configuration (%)	Mulliken charge analysis (B3LYP)				
						metal	phen	phz	linker	donor
1a	402 (1.93)	405 (0.362)	H→L (97)	345 (0.616)	H→L (86)		18→34 (16)	38→63 (25)	41→3 (-38)	3→0 (-3)
	387 (1.58)	362 (0.166)	H-1→L (91)	321 (0.143)	H-1→L (82)		53→36 (-17)	39→60 (21)	7→4 (-3)	1→0 (-1)
	302 (4.62)	307 (1.144)	H→L+1 (74)	277 (0.261)	H-2→L (55)		23→62 (39)	36→33 (-3)	38→4 (-34)	3→0 (-3)
	289 (5.18)									
2a	395 (2.56)	385 (0.279)	H→L (96)	336 (0.690)	H-1→L (12), H→L (74)		35→32 (-3)	46→60 (14)	16→7 (-9)	3→1 (-2)
	376 (2.16)	365 (0.358)	H-1→L (91)	322 (0.101)	H-1→L (72), H→L (13)		57→32 (-25)	36→58 (22)	7→8 (1)	1→2 (1)
	300 (6.43)	307 (1.445)	H→L+1 (85)	277 (0.595)	H-2→L (53), H→L+1 (25)		37→37 (0)	45→31 (-14)	15→25 (10)	2→7 (5)
	289 (6.79)			270 (1.066)	H-2→L (29), H→L+1 (41)					
1b	412 (2.10)	441 (0.747)	H→L (98)	365 (1.181)	H→L (85)		12→32 (20)	27→60 (33)	60→8 (-52)	2→0 (-2)
	399 (1.87)									
	310 (4.24)	340 (0.434)	H-2→L (35), H→L+1 (50)	292 (1.098)	H-2→L (17), H-1→L (12), H-1→L+1 (11), H→L+1 (42)		34→45 (11)	26→44 (18)	38→11 (-27)	2→0 (-2)
	299 (4.26)	332 (1.033)	H-2→L (51), H→L+1 (38)							
2b	406 (2.94)	417 (0.996)	H→L (97)	359 (1.414)	H→L (87)		19→29 (10)	34→54 (20)	44→16 (-28)	3→2 (-1)
	387 (2.33)	376 (0.105)	H-1→L (92)	325 (0.044)	H-1→L (75)		61→28 (-33)	34→53 (19)	5→16 (11)	0→2 (2)
	313 (5.13)	340 (0.895)	H-3→L (18), H→L+1 (69)	298 (1.021)	H-2→L (17), H→L+1 (58)		30→24 (-6)	32→34 (2)	35→35 (0)	3→7 (4)
	299 (4.81)	334 (0.423)	H-3→L (70), H→L+1 (22)	276 (0.235)	H-4→L (18), H-2→L (52), H→L+1 (13)		53→27 (-26)	25→48 (23)	20→22 (2)	2→3 (1)
[ReCl(CO)$_3$(**1a**)]	412 (2.33)	424 (0.272)	H-2→L (97)	355 (0.700)	H-2→L (15), H-1→L (59)	12→0 (-12)	8→37 (29)	30→60 (30)	46→3 (-43)	3→0 (-3)
	396 (2.12)	333 (0.798)	H-4→L (21), H-2→L+2 (59)			13→0 (-13)	13→67 (54)	32→30 (-2)	39→2 (-37)	2→0 (-2)
	316 (4.58)	284 (0.833)	H-9→L (21), H-9→L+1 (24), H-4→L+2 (35)	277 (0.845)	H-4→L+2 (10), H-1→L+2 (23), H→L+2 (21)	37→3 (-34)	24→72 (48)	29→24 (-5)	9→2 (-7)	1→0 (-1)
	302 (7.14)									
[ReCl(CO)$_3$(**2a**)]	401 (1.79)	390 (0.247)	H-3→L (41), H-2→L (51)	348 (0.585)	H-2→L (14), H-1→L (37), H-1→L+1 (39)	45→0 (-45)	10→35 (25)	28→59 (31)	14→5 (-9)	2→1 (-1)
	384 (1.89)									
	297 (7.09)	315 (1.170)	H-4→L (10), H-3→L+2 (11), H-2→L+2 (57)	275 (1.246)	H-4→L+2 (11), H-2→L+1 (13), H-2→L+2 (27)	28→0 (-28)	18→62 (44)	34→30 (-4)	17→6 (-11)	3→1 (-2)
[ReCl(CO)$_3$(**1b**)]	424 (1.91)	472 (0.698)	H→L (90)	376 (1.236)	H→L (83)	8→0 (-8)	8→35 (27)	22→58 (36)	60→7 (-53)	2→0 (-2)
	396 (1.74)									
	326 (2.91)	352 (0.771)	H-4→L (73), H→L+2 (22)	295 (1.531)	H-4→L (17), H-4→L+2 (11), H→L+2 (36), H→L+3 (17)	1→0 (-1)	28→44 (16)	50→49 (-1)	20→6 (-14)	1→0 (-1)
	308 (4.22)									
	283 (5.68)			268 (0.136)	H-6→L (11), H-4→L+1 (36)					
[ReCl(CO)$_3$(**2b**)]	411 (3.28)	471 (0.135)	H-1→L (96)	366 (1.456)	H-2→L (30), H-1→L (52)	89→0 (-89)	6→34 (28)	2→54 (52)	2→11 (9)	0→1 (1)
	396 (3.09)	431 (0.836)	H-2→L (97)			5→0 (-5)	10→32 (22)	30→56 (26)	51→11 (-40)	4→1 (-3)

Continued on next page

Compound	λ (ε) / nm (10^{-4} $M^{-1}cm^{-1}$)	B3LYP (f) / nm	MO configuration (%)	CAM B3LYP (f) / nm	MO configuration (%)	Mulliken charge analysis (B3LYP)				
						metal	phen	phz	linker	donor
	318 (7.52) 305 (7.45)	344 (1.457)	H-4→L (25), H-2→L+2 (66)	298 (1.308) 255 (0.163)	H-2→L+2 (34), H-1→L+2 (11) H-2→L+7 (11), H-1→L+7 (23)	7→0 (-7)	17→50 (33)	36→33 (-3)	37→15 (-22)	3→2 (-1)



(a) [ReCl(CO)$_3$(**1a**)] H-4 **(b)** [ReCl(CO)$_3$(**1a**)] H-2 **(c)** [ReCl(CO)$_3$(**1a**)] LUMO

(d) [ReCl(CO)$_3$(**2a**)] H-3 **(e)** [ReCl(CO)$_3$(**2a**)] LUMO **(f)** [ReCl(CO)$_3$(**2a**)] L+2

(g) [ReCl(CO)$_3$(**1b**)] HOMO **(h)** [ReCl(CO)$_3$(**1b**)] LUMO **(i)** [ReCl(CO)$_3$(**1b**)] L+2

(j) [ReCl(CO)$_3$(**2b**)] H-2 **(k)** [ReCl(CO)$_3$(**2b**)] H-1 **(l)** [ReCl(CO)$_3$(**2b**)] LUMO

Fig. 6 Examples of molecular orbitals predicted to be involved in strong transitions (B3LYP, CH_2Cl_2 solvent field).