Electronic supplementary information

Unusual azobenzene/bipyridine palladacycles: structural, dynamical, photophysical and theoretical studies

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Table S1 ^{1}H NMR data of complexes **1a-4a** in DMSO-d_6 and DMF-d_7 and/or CD_2Cl_2 at room temperature (δ / ppm, J / Hz).

H	1a	2a (α and β)	3a	4a	solvent
3	7.94 d $^3J(HH)$=7.6	7.49 s, 7.50 s	6.81 s	7.00 s	DMSO-d_6
	7.94 d $^3J(HH)$=7.6	7.67 s, 7.60 s	7.08 s	7.13 s	DMF-d_7
			7.06 s	7.18 s	CD_2Cl_2
4	7.28 t $^3J(HH)$=7.4	-	-	-	DMSO-d_6
	7.30 t $^3J(HH)$=7.5				DMF-d_7
5	7.21 t $^3J(HH)$=7.7	7.09 d, 7.07 d $^3J(HH)$=7.8, 8.0	6.35 d $^3J(HH)$=8.7	6.63 d $^3J(HH)$=8.6	DMSO-d_6
	7.21 t $^3J(HH)$=7.7	7.09 d, 7.11 $^3J(HH)$=7.6, 7.6	6.49 d $^3J(HH)$=8.6	6.67 d $^3J(HH)$=9.1	DMF-d_7
			6.43 d $^3J(HH)$=8.4	6.53 d $^3J(HH)$=9.1	CD_2Cl_2
6	7.70 d $^3J(HH)$=7.8	7.80 d, 7.38 d $^3J(HH)$=7.9, 8.1	7.48 d $^3J(HH)$=8.0	7.66 d $^3J(HH)$=8.7	DMSO-d_6
	7.70 d $^3J(HH)$=7.6	7.82 d, 7.45 $^3J(HH)$=7.9, 8.0	7.56 d $^3J(HH)$=8.6	7.70 d $^3J(HH)$=9.0	DMF-d_7
			7.65 d $^3J(HH)$=8.4	7.69 d $^3J(HH)$=8.9	CD_2Cl_2
9	7.69 d $^3J(HH)$=7.3	7.67 d, 7.68 d $^3J(HH)$=7.5, 7.9	7.50 d $^3J(HH)$=7.7	8.34 s	DMSO-d_6
	7.69 d $^3J(HH)$=7.2	7.77 d, 7.84 d $^3J(HH)$=7.6, 7.9	7.61 d $^3J(HH)$=8 8	8.48 s	DMF-d_7
			7.58 d $^3J(HH)$=7.2	8.42 s	CD_2Cl_2
10	7.36 t $^3J(HH)$=7.4	7.33 t, 7.18 t $^3J(HH)$=7.3, 7.5	7.16 t $^3J(HH)$=7.1	-	DMSO-d_6
	7.36 t $^3J(HH)$=7.0	7.36 t, 7.18 t $^3J(HH)$=7.5, 7.6	7.19 t $^3J(HH)$=9.3		DMF-d_7
			7.25 t $^3J(HH)$=7.1		CD_2Cl_2
11	7.27 t $^3J(HH)$=7.2	7.25 t, 7.26 t $^3J(HH)$=7.3, 7.1	7.15 t $^3J(HH)$=7.0	8.02 d $^3J(HH)$=8.5	DMSO-d_6
	7.28 t $^3J(HH)$=7.5	7.29 t, 7.27 t $^3J(HH)$=7.7, 74	7.19 t $^3J(HH)$=9.3	8.09 d $^3J(HH)$=8.8	DMF-d_7
			7.22 t $^3J(HH)$=7.2	8.20 d $^3J(HH)$=9.0	CD_2Cl_2
12	7.50 d $^3J(HH)$=7.9	7.43 d, 7.90 d $^3J(HH)$=8.0, 7.8	7.30 d $^3J(HH)$=7.1	7.53 d $^3J(HH)$=8.7	DMSO-d_6
	7.50 d $^3J(HH)$=7.9	7.51 d, 7.92 d $^3J(HH)$=8.0, 7.7	7.40 d $^3J(HH)$=9.4	7.61 d $^3J(HH)$=8.7	DMF-d_7
			7.46 d $^3J(HH)$=7.5	7.61 d $^3J(HH)$=8.9	CD_2Cl_2
NH_2	-	-	6.78 s	-	DMSO-d_6
			6.79 s		DMF-d_7
			4.47 s		CD_2Cl_2
CH_3	-	2.29 s, 2.39 s	-	3.17 s	DMSO-d_6
		2.31 s, 2.42 s		3.17 s	DMF-d_7
				3.17 s	CD_2Cl_2
b	8.65 d $^3J(HH)$=8.0	8.65 d $^3J(HH)$=8.0	8.64 d br $^3J(HH)$=8.1	8.65 d $^3J(HH)$=8.1	DMSO-d_6
	8.73 d $^3J(HH)$=8.0	8.72 d $^3J(HH)$=8.1	8.69 d br $^3J(HH)$=8.3	8.73 d $^3J(HH)$=8.0	DMF-d_7
			8.19 d br $^3J(HH)$=7.8	8.20 d br $^3J(HH)$=8.1	CD_2Cl_2
c	8.30 t br $^3J(HH)$=7.4	8.30 t br $^3J(HH)$=7.4	8.25 t br $^3J(HH)$=7.4	8.30 t br $^3J(HH)$=7.4	DMSO-d_6
	8.30 t br $^3J(HH)$=7.4	8.36 s br	8.25 s br	8.37 t $^3J(HH)$=7.3	DMF-d_7
			7.98 t $^3J(HH)$=7.9	8.07 t $^3J(HH)$=7.7	CD_2Cl_2
d	-	-	7.30 t $^3J(HH)$=6.0	7.34 t $^3J(HH)$=7.0	CD_2Cl_2
e	-	-	7.91 d br $^3J(HH)$=6.0	7.86 d br $^3J(HH)$=6.4	CD_2Cl_2
b'	8.65 d $^3J(HH)$=8.0	8.65 d $^3J(HH)$=8.0	8.64 d br $^3J(HH)$=8.1	8.65 d $^3J(HH)$=8.1	DMSO-d_6
	8.65 d $^3J(HH)$=8.0	8.72 d $^3J(HH)$=8.1	8.69 d br $^3J(HH)$=8.3	8.73 d $^3J(HH)$=8.0	DMF-d_7
			8.19 d br $^3J(HH)$=8.2	8.20 d br $^3J(HH)$=8.1	CD_2Cl_2
c'	8.30 t br $^3J(HH)$=7.4	8.30 t br $^3J(HH)$=7.4	8.25 t br $^3J(HH)$=7.4	8.30 t br $^3J(HH)$=7.4	DMSO-d_6
	8.30 t br $^3J(HH)$=7.4	8.36 s br	8.25 s br	8.37 t $^3J(HH)$=7.3	DMF-d_7
			8.07 t $^3J(HH)$=7.9	8.12 t $^3J(HH)$=8.0	CD_2Cl_2
d'	-	-	overlapped with H-6	overlapped with H-6	CD_2Cl_2
e'	-	-	9.18 d br, $^3J(HH)$=6.0	9.22 d br, $^3J(HH)$=6.0	CD_2Cl_2

Table S2 ^{13}C NMR data of complexes **1a**-**4a** in DMSO-d_6 at room temperature (δ/ ppm, J / Hz).

C	1a	2a	3a	4a
1	155.7	161.6 (α) 154.7 (β)	152.7	152.6
2	163.7	155.9 (α) 147.0 (β)	161.3	161.9
3	128.3	136.6 (α) 135.5 (β)	119.4	117.2
4	125.8	141.8 (α) 140.7 (β)	152.1	151.6
5	130.8	126.5 (α) 126.3 (β)	110.7	110.0
6	135.3	128.2 (α) 120.3 (β)	130.9	131.0
7	156.5	156.4 (α) 163.7 (β)	143.9	160.6
8	146.6	146.2 (α) 155.5 (β)	156.2	144.8
9	135.1	135.2 (α) 135.1 (β)	119.7	129.9
10	130.4	130.1 (α) 130.4 (β)	124.9	144.6
11	125.4	125.3 (α) 125.7 (β)	127.8	120.9
12	120.7	120.5 (α) 128.0(β)	134.7	120.0
CH_3	-	21.9 (α) 20.1 (β)	-	40.1
b,b'	124.9	124.2 α and β	124.3	123.6
c,c'	141.0	140.7 α and β	140.6	140.7

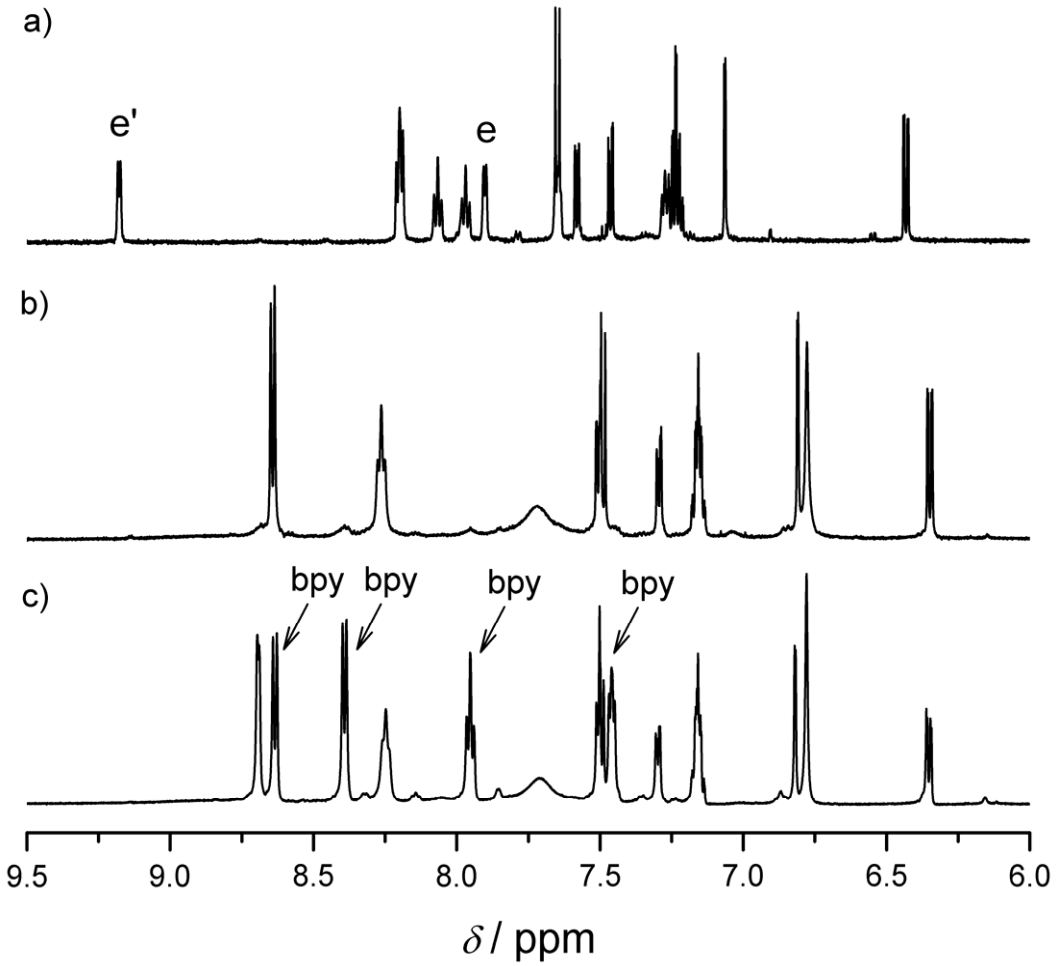


Fig. S1. ^{1}H NMR spectra of **3a** a) in CD_2Cl_2, b) in DMSO-d_6. The spectrum in c) was obtained by dissolving **3b** in DMSO-d_6 (whereby it converts to **3a** and free bpy). All spectra were recorded at 25 ºC.

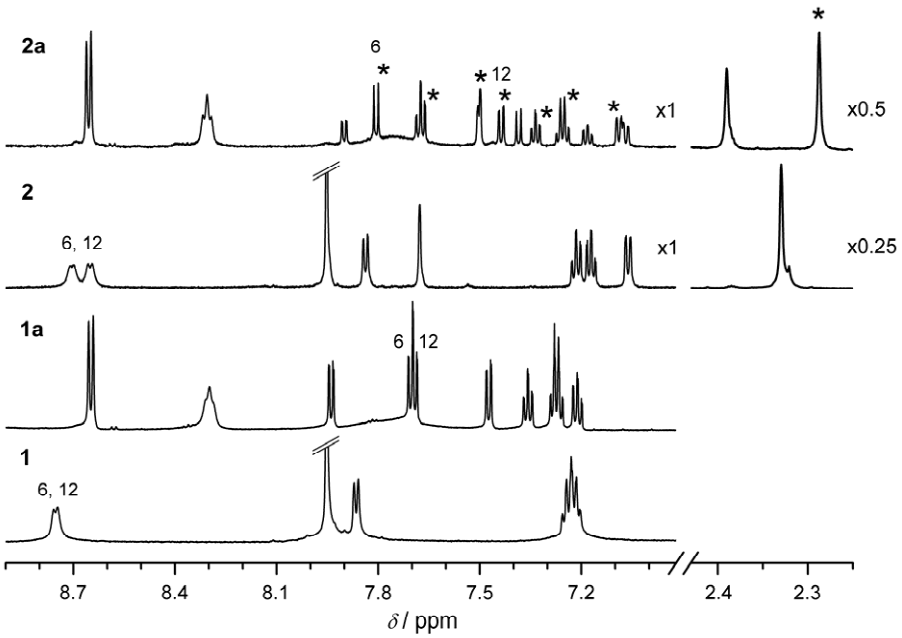


Fig. S2. ^{1}H NMR spectra of complexes **1**, **1a**, **2** and **2a** in DMSO-d_6. The signals of alpha isomer of complex **2a** are denoted by a star (*).

Table S3 Crystallographic data, collection and structure refinement data.

Compound	**1a**	**2a**	**3a**	**4a**	**3b1**	**3b2**
Empirical formula	$C_{22}H_{16}Cl_2N_4Pd_2$	$C_{23}H_{18}N_4Cl_2Pd_2$	$C_{26}H_{29}Cl_2N_5O_2Pd_2S_2$	$C_{24}H_{20}Cl_2N_6O_2Pd_2$	$C_{36}H_{39}Cl_2N_7O_3Pd_2S_2$	$C_{37}H_{29}Cl_2N_8O_{2.5}Pd_2$
Formula wt. / g mol^{-1}	619.32	634.11	792.37	708.16	965.58	909.39
Crystal dimensions / mm	0.18 x 0.10 x 0.06	0.14 x 0.07 x 0.02	0.18 x 0.14 x 0.13	0.15 x 0.07 x 0.05	0.18 x 0.12 x 0.08	0.18 x 0.07 x 0.03
Space group	$P\bar{1}$	$P\bar{1}$	*P bca*	$P2_1/c$	$P\bar{1}$	*C* 2/*m*
a / Å	10.2884(5)	10.0962(4)	14.9012(2)	11.0479(1)	7.7652(2)	19.2858(9)
b / Å	10.6609(8)	10.9626(3)	15.388(2)	17.4881(1)	14.9221(3)	26.7698(8)
c / Å	11.6302(5)	11.9130(5)	26.0962(4)	13.3450(1)	17.6810(4)	17.6814(6)
α / °	107.874(5)	107.167(3)	90	90	99.709(2)	90
β / °	100.279(4)	108.457(3)	90	104.940(1)	94.075(2)	122.432(2)
γ / °	114.134(5)	105.761(3)	90	90	96.168(2)	90
Z	2	2	8	4	2	8
V / Å^3	1037.9 (2)	1093.75(9)	5983.9(7)	2491.19(3)	1999.39(8)	7704.7(5)
D_{calc} / g cm^{-3}	1.984	1.925	1.759	1.888	1.604	1.568
Diffractometer type	CAD-4	Xcalibur Nova	Xcalibur	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova
Wavelength / Å	1.54179 (CuK_α)	1.54179 (CuK_α)	0.71073 (MoK_α)	1.54179 (CuK_α)	1.54179 (CuK_α)	1.54179 (CuK_α)
μ / mm^{-1}	16.488	15.662	1.554	13.921	9.823	9.109
Absorption correction	Psi-scans	Multi-scans	Multi-scans	Multi-scans	Multi-scans	Multi-scans

T_{min}, T_{max}	0.0239, 0.0971	0.434, 0.731	0.751, 0.817	0.61412, 1.000	0.280, 0.456	0.5701, 1.000
Θ range / °	4.26 - 76.20	4.31 – 76.28	2.46 – 27.48	4.14 – 76.11	2.55 – 76.21	4.59 – 76.48
Range of h, k, l	$12 > h > 0$;	$12 > h > -12$;	$19 > h > -19$;	$13 > h > -13$;	$9 > h > -9$;	$17 > h > -24$;
	$12 > k > -13$;	$13 > k > -13$;	$19 > k > -19$;	$21 > k > -21$;	$18 > k > -18$;	$33 > k > -33$;
	$14 > l > -14$	$14 > l > -14$	$33 > l > -33$	$14 > l > -16$	$20 > l > -22$	$22 > l > -21$
Reflections collected	4592	9446	53697	13421	17952	21812
Independent reflections	4341	4437	6856	5094	8372	8032
Observed reflections ($I \geq 2\sigma$)	3193	3720	5353	4502	6919	6351
R_{int}	0.0364	0.0727	0.0478	0.0209	0.0303	0.0299
R (F)	0.0541	0.0766	0.0647	0.0296	0.0401	0.0466
R_w (F^2)	0.1441	0.2248	0.1391	0.0954	0.1126	0.1555
Goodness of fit	1.035	1.042	1.161	1.122	1.033	1.046
No. of parameters	271	281	362	327	475	501
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (eÅ^{-3})	1.126; -2.461	2.136; -1.599	1.716; -0.551	0.766; -0.566	1.175; -0.420	1.208; -1.320

Table S4 Cremer and Pople Puckering Parameters for the six-membered ring Pd(1)-Cl(1)-Pd(2)-C(8)-C(7)-N(1) of complexes **1a**-**4a**.

Compound	Q (Å)	θ (°)	φ (°)
1a	1.325(4)	61.1(3)	88.0(3)
2a	1.339(5)	61.1(3)	88.1(4)
3a	1.307(3)	60.5(2)	87.5(2)
4a	1.425 (2)	57.1(1)	76.1(2)

Table S5 Geometric parameters of the hydrogen bonds.

	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
1a	C3-H3···Cl2	0.93	2.76	3.29 (1)	117
	C3-H3···Cl2[a]	0.93	2.78	3.66 (1)	158
	C3-H3···Cl2[b]	0.93	2.79	3.51(1)	134
2a	C3-H3···Cl2	0.93	2.75	3.28 (1)	117
	C3-H3···Cl2	0.93	2.68	3.59 (1)	169
3a	N5-H1N···O1	0.89(7)	2.00(7)	2.886(9)	175(8)
	N5-H2N···O2	0.89(8)	1.99(8)	2.859(8)	168(8)
	C3-H3···Cl2	0.95	2.71	3.259(6)	117
	C21-H21···O2[d]	0.95	2.32	3.16 (1)	146
	C24-H24C···Cl2[e]	0.98	2.81	3.73 (1)	158
4a	C3-H3···Cl2	0.93	2.80	3.298(4)	114
	C16-H16···Cl2[f]	0.93	2.83	3.734(5)	166
	C19-H19···Cl2[f]	0.93	2.59	3.481(5)	162
	C24-H24A···O1[g]	0.96	2.56	3.393(9)	146
3b1	N7-HN1···O2[h]	0.85(5)	2.00(5)	2.834(9)	164(4)
	N7-HN2···Cl2	0.88(4)	2.50(5)	3.329(6)	158(5)
	O3-OH1···Cl2[i]	0.82	2.35	3.171(9)	174
	C14-H14···O1[a]	0.93	2.54	3.392(9)	152
	C16-H16···Cl2[j]	0.93	2.77	3.671(5)	163
	C19-H19···Cl2[j]	0.93	2.75	3.655(5)	165
	C21-H21···N2[k]	0.93	2.55	3.476(5)	178
	C24-H24···O3	0.93	2.52	3.31(1)	142
	C33-H33C···Cl2[l]	0.96	2.79	3.682(7)	156
	C36-H36B···O2[h]	0.96	2.58	3.47(1)	155
3b2	N7-H7A···Cl3	0.86	2.62	3.382(9)	149
	N7-H7B···Cl2	0.86	2.47	3.305(8)	165
	C13-H13···Cl1	0.93	2.74	3.327(6)	122
	C16-H16···O4	0.93	2.34	3.25(1)	165
	C16-H16···O4[m]	0.93	2.41	3.32(1)	163
	C19-H19···O4[m]	0.93	2.57	3.45(1)	154
	C26-H26-Cl1[n]	0.93	2.82	3.718(6)	163
	C34-H34···O2[o]	0.93	2.45	3.36(2)	164
	C36-H36···N9	0.93	2.57	2.87 (2)	100
	C39-H39···N8	0.93	2.44	2.79(2)	102
	C41-H41···Cl2[p]	0.93	2.74	3.66(2)	170

Symmetry code:
(a) 1-x,1-y,1-z; (b) -x,1-y,1-z; (c) 1-x,-y,2-z; (d) x,1/2-y,1/2+z; (e) 2-x,1/2+y,1/2-z; (f) 2-x,-y,1-z; (g) 2-x,-1/2+y,1/2-z; (h) 1-x,1-y,-z; (i) -x,2-y,1-z; (j) 1+x,y,z; (k) 1-x,-y,-z; (l) x,-1+y,z; (m) 2-x,y,1-z; (n) 1/2+x,3/2-y,z; (o) 3/2-x,-1/2+y,1-z; (p) 1/2+x,-1/2+y,z

Table S6 Analysis of short ring interactions.

		Cg(I)···Cg(J) (Å)	α (º)	β (º)	Cg(I)_perp (Å)	Cg(J)_perp (Å)
1a	Cg(4)···Cg(5)[a]	3.715(6)	3.6(5)	21.31	3.461(4)	3.461(4)
3a	Cg(2)···Cg(4)[b]	3.687(3)	1.3(3)	19.98	3.492(2)	3.466(3)
	Cg(4)···Cg(5)[b]	3.670(4)	2.3(3)	19.86	3.483(3)	3.453(3)
4a	Cg(6)···Cg(6)[b]	3.793(3)	0	25.14	3.337(2)	3.516(2)
	Cg(7)···Cg(7)[c]	3.685(2)	0	16.10	3.541(2)	3.541(2)
3b1	Cg(1)···Cg(3)	3.544(2)	26.9(2)	18.61	3.069(1)	3.359(2)
	Cg(2)···Cg(3)[d]	3.680(2)	9.3(2)	16.72	3.594(2)	3.524 (1)
	Cg(4)···Cg(8)[e]	3.745(3)	8.6(2)	16.36	3.407(2)	3.593(2)
3b2	Cg(9)···Cg(3)	3.361(2)	10.4(2)	7.43	3.279(2)	3.333(2)
	Cg(3)···Cg(3)[f]	3.609(2)	0	18.89	3.414(2)	3.414(2)
	Cg(4)···Cg(5)[f]	3.673(3)	4.7(2)	21.46	3.493(2)	3.419(2)
	Cg(4)···Cg(6)	3.656(3)	3.5(2)	20.20	3.429(2)	3.431(2)
	Cg(5)···Cg(10)	3.581(3)	12.2(2)	22.97	3.423(2)	3.297(2)

α = Dihedral angle between planes I and J
β = Angle Cg(I)-->Cg(J) vector and normal to plane I
Cg···Cg = Distance between ring centroids
Cg(I)_Perp = Perpendicular distance of Cg(I) on ring J
Cg(J)_Perp = Perpendicular distance of Cg(J) on ring I

Symmetry code:
(a) –x, 1-y, 1-z; (b) 2-x, -y, 1-z; (c) 1-x, y, z; (d) x-1, y, z; (e) 1+x, y, z; (f) 3/2-x,3/2-y,1-z.

Atoms defining rings:
(1) Pd1, N1, N2, C1, C2; (2) Pd2, N3, C17, C18, N4; (3) Pd2, N3, C17, C18, N4; (4) N3, C13, C14, C15, C16, C17; (5) N4, C18, C19, C20, C21, C22; (6) N3, C13, C14, C15, C16, C17; (7) C1, C2, C3, C4, C5, C6; (8) N5, C23, C24, C25, C26, C27; (9) Pd1, N5, C27, C28, N6; (10) N6, C28, C29, C30, C31, C32

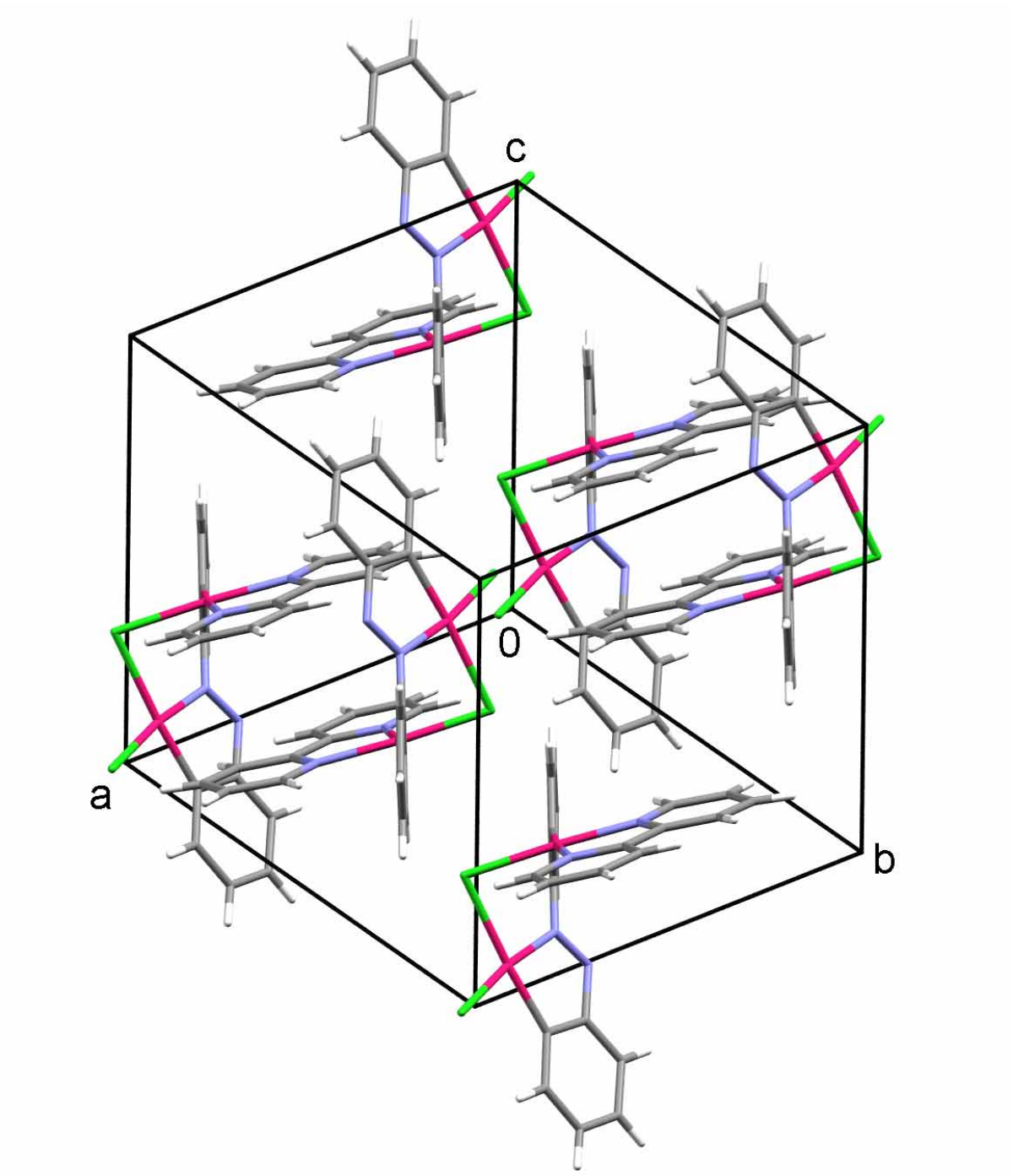


Fig. S3. Packing of **1a** in the unit cell.

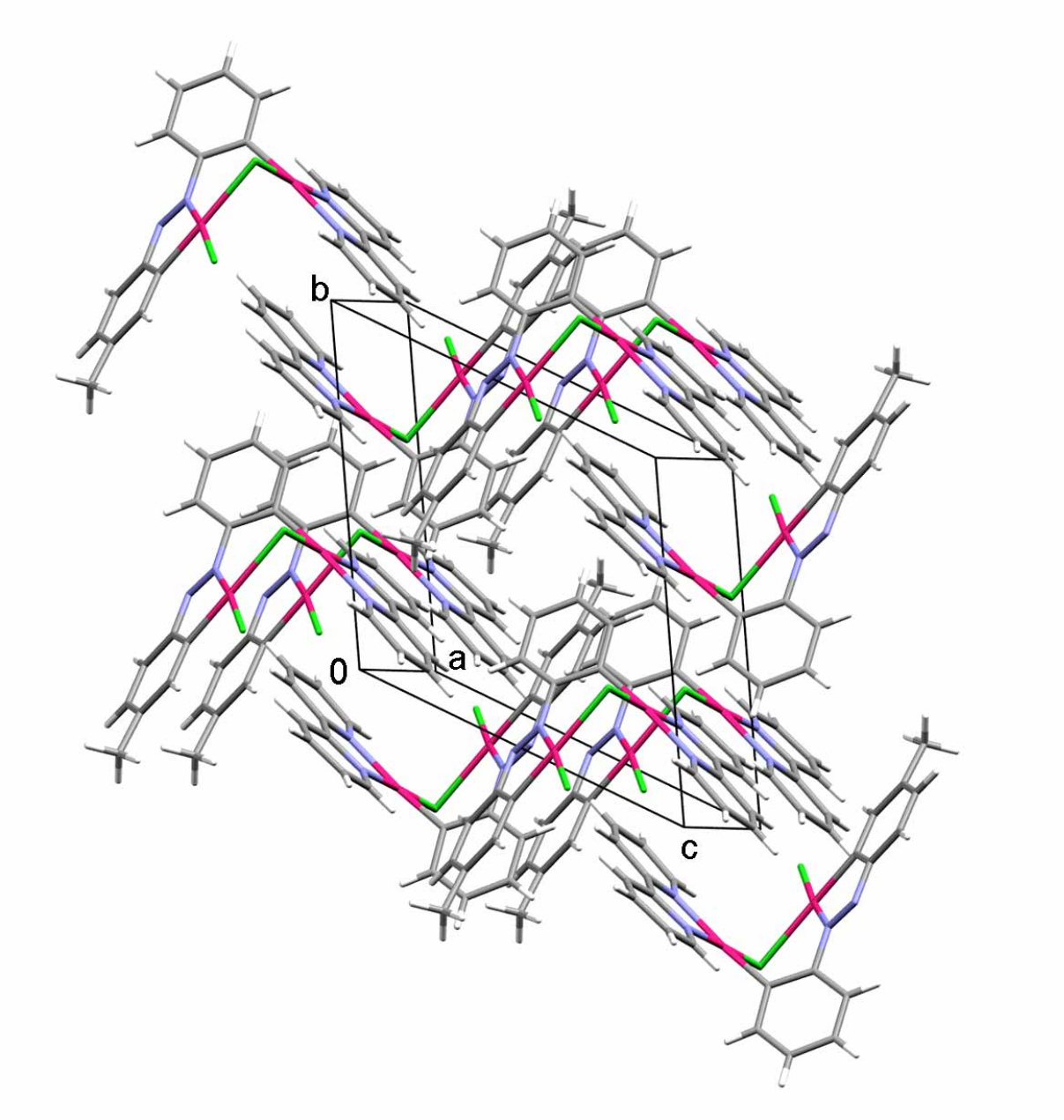


Fig. S4. Packing of **2a** in the unit cell.

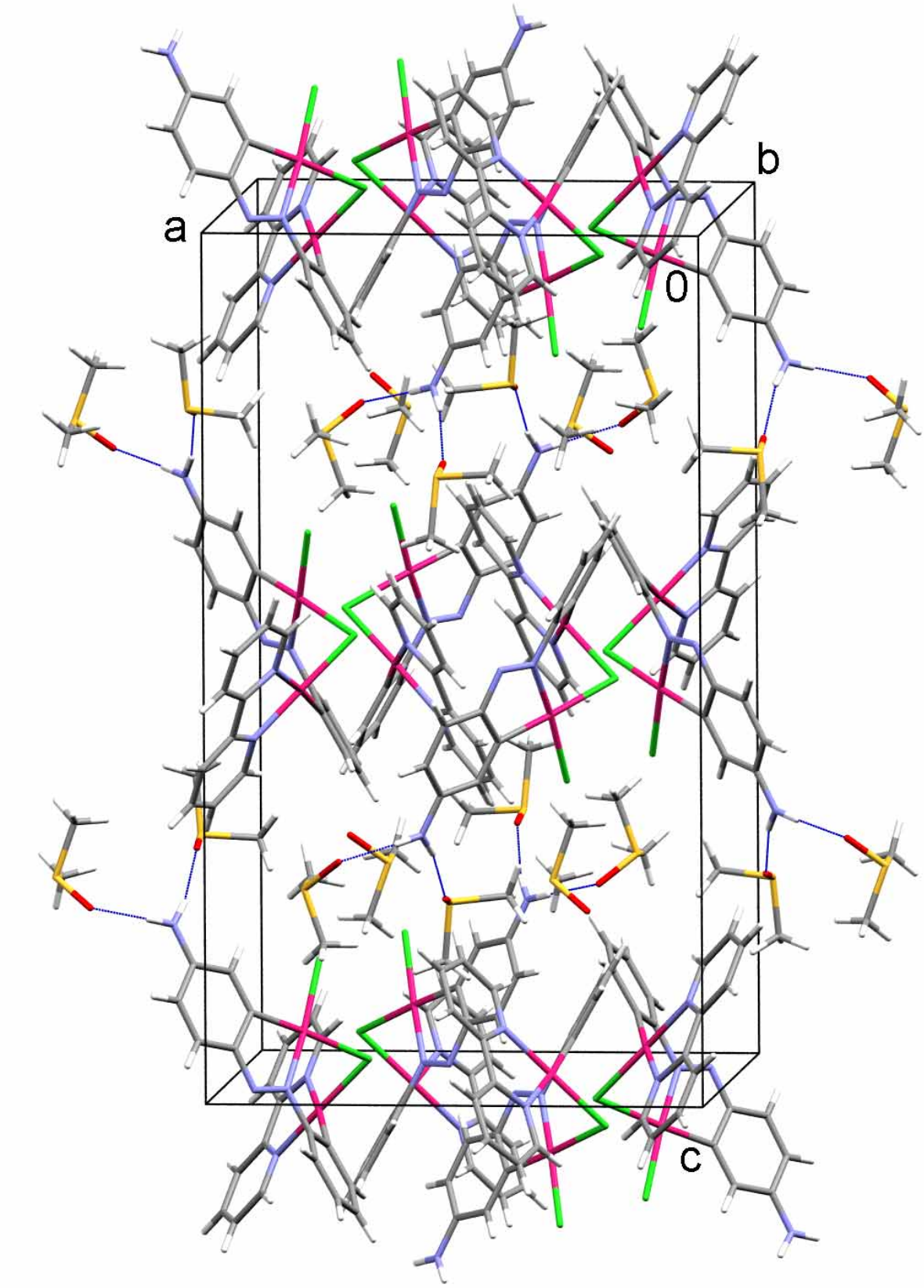


Fig. S5. Packing of **3a** in the unit cell. Hydrogen bonds are shown by blue dashed lines.

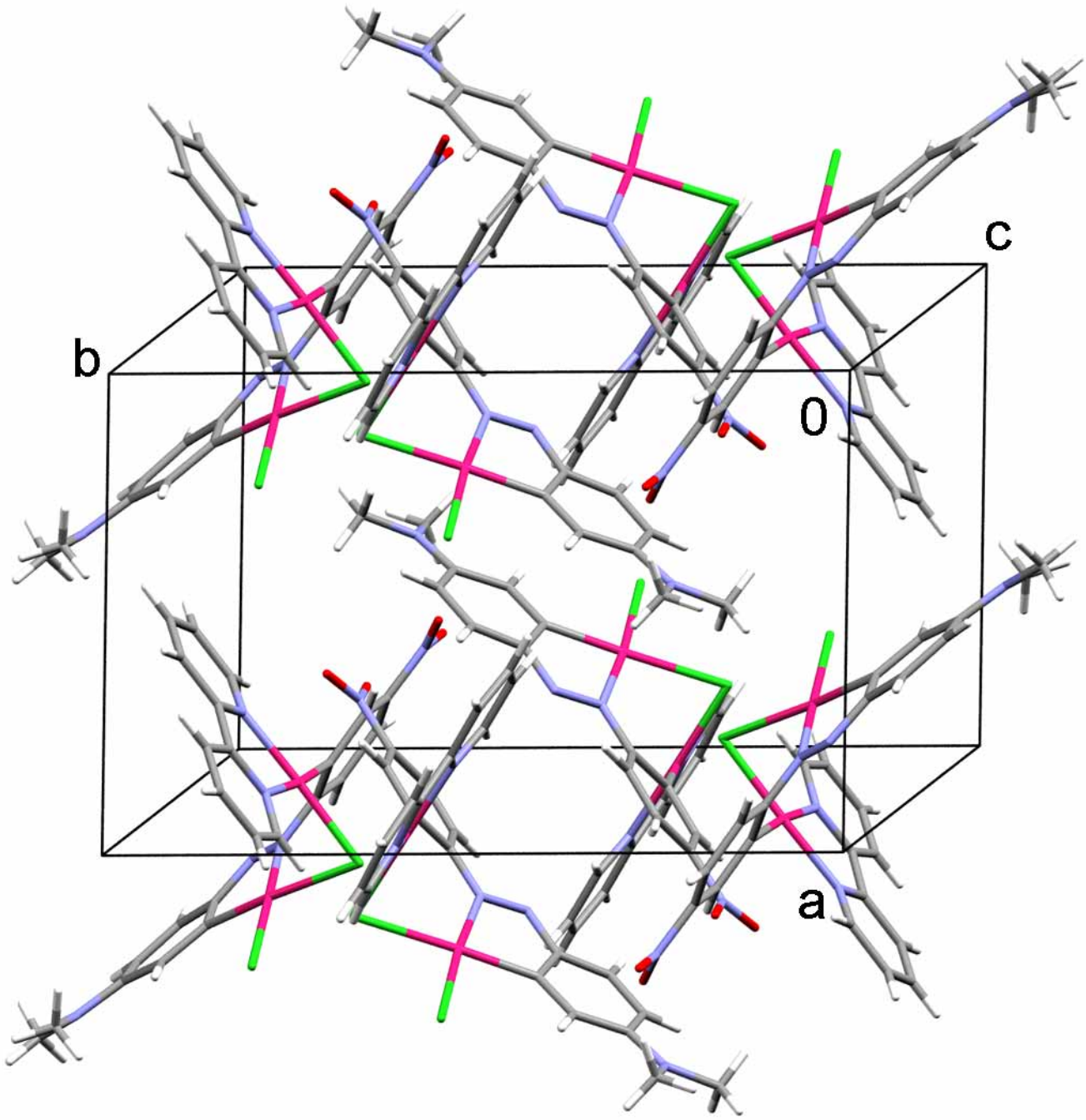


Fig. S6. Packing of **4a** in the unit cell.

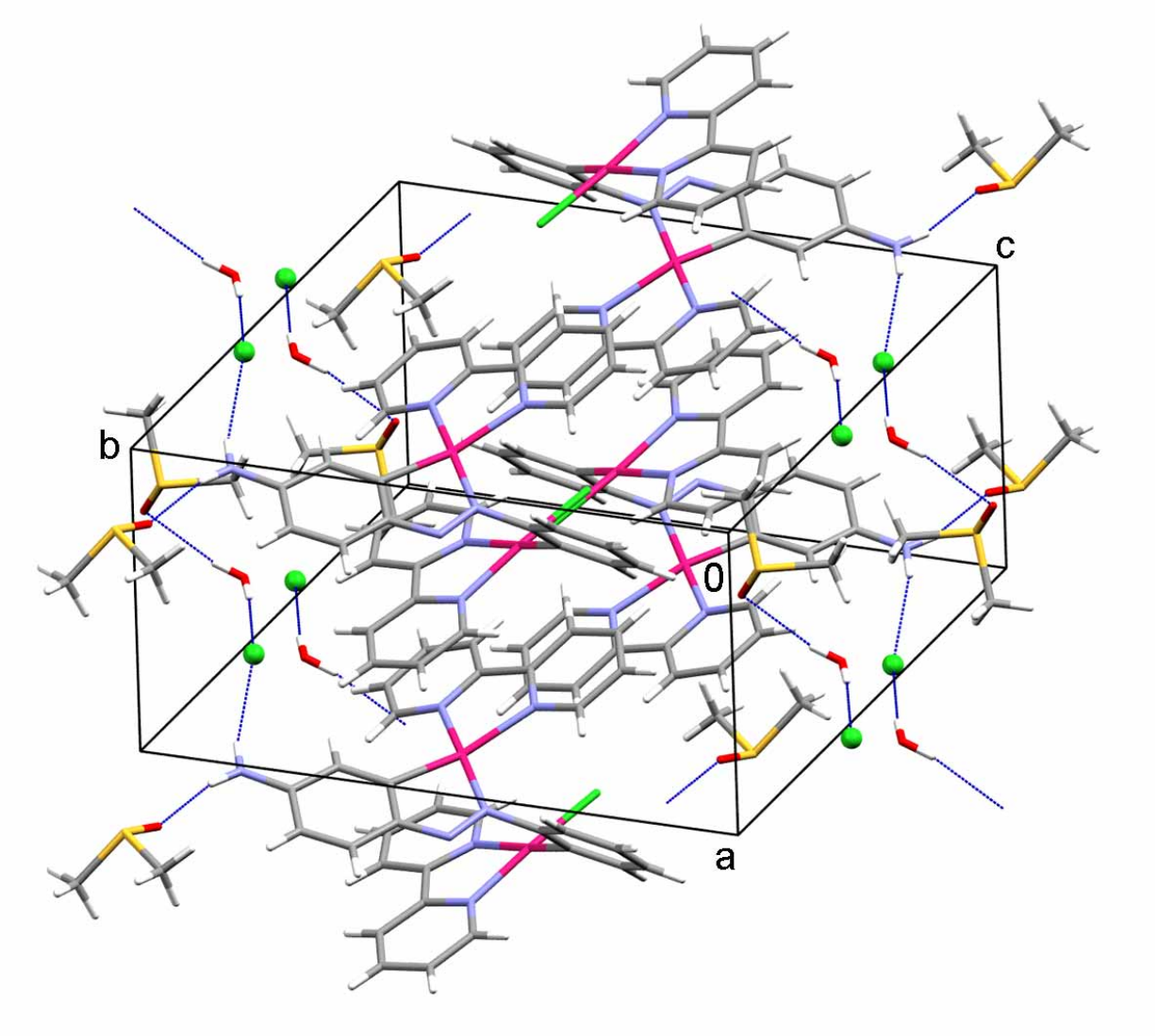


Fig. S7. Packing of **3b1** in the unit cell. Hydrogen bonds are shown by blue dashed lines. Green spheres represent chloride ions.

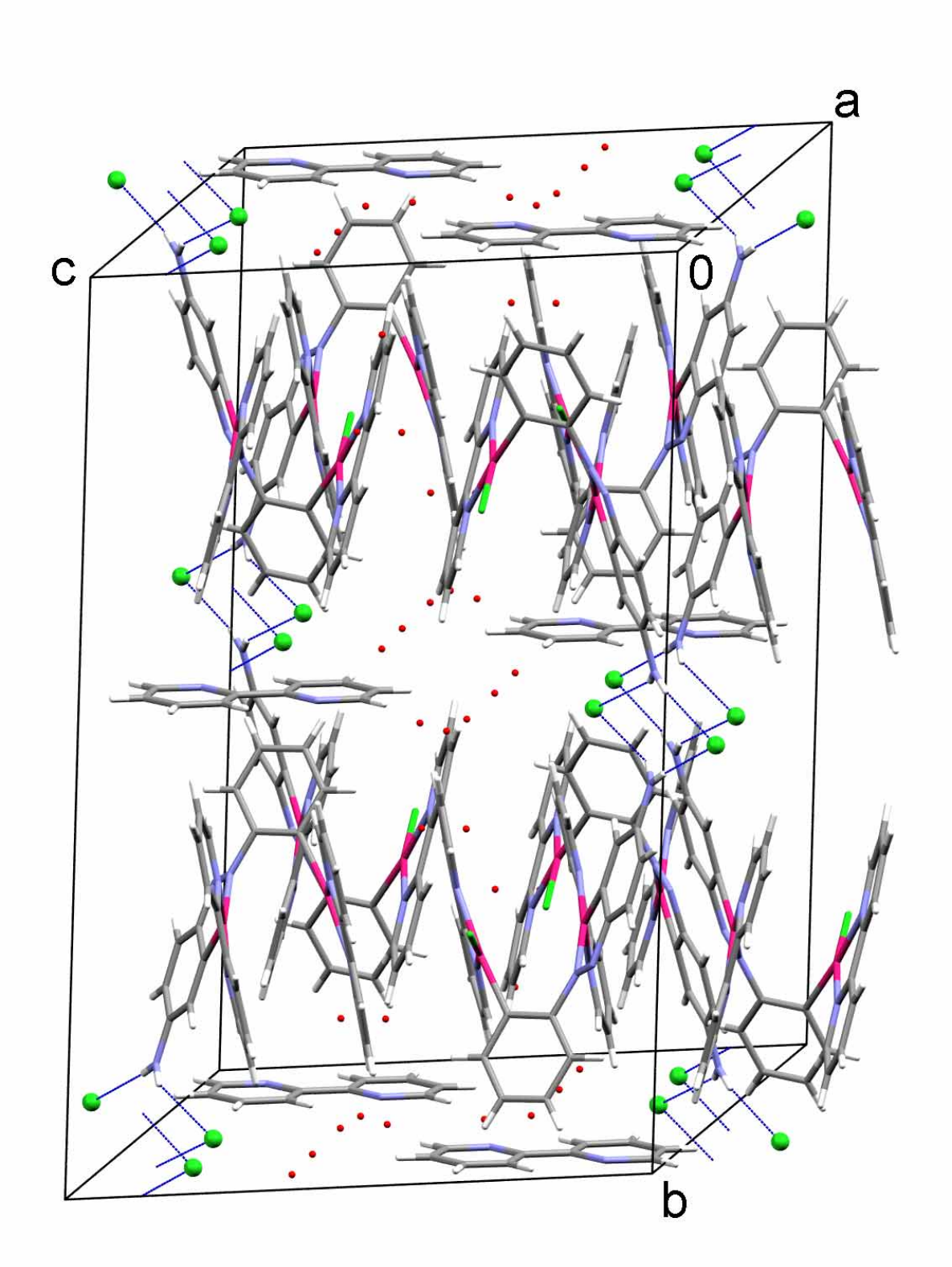


Fig. S8. Packing of **3b2** in the unit cell. Hydrogen bonds are shown by blue dashed lines. Green spheres represent chloride ions.

Table S7 Bond distances (in Ångströms) and bond angles (in degrees) around Pd atoms from X-ray diffraction and gas phase DFT calculation for alpha isomers.

	1a		**2a**		**3a**		**4a**		**3b-I**	**3b-II**	**3b**
	exp	calc	exp	calc	exp	calc	exp	calc	exp	exp	calc
Pd1–C2	1.961(8)	1.974	1.960(8)	1.974	1.972(6)	1.973	1.962(4)	1.973	1.995(3)	1.991(5)	2.009
Pd1–N1	2.032(8)	2.077	2.034(6)	2.078	1.984(5)	2.079	2.027(3)	2.078	2.009(3)	2.006(4)	2.048
Pd1–Cl1/N5	2.479(2)	2.574	2.4777(19)	2.575	2.467(2)	2.570	2.518 (1)	2.563	2.066(3)	2.065(4)	2.103
Pd1–Cl2/N6	2.305(2)	2.339	2.306(2)	2.341	2.312(2)	2.349	2.312(1)	2.348	2.134(3)	2.125(4)	2.193
Pd2–C8	1.967(8)	1.999	1.965(8)	1.999	1.986(6)	1.999	1.995(4)	2.001	1.993(4)	1.998(4)	2.005
Pd2–N3	2.104(7)	2.153	2.125(7)	2.154	2.109(5)	2.156	2.111(3)	2.149	2.121(3)	2.100(4)	2.157
Pd2–N4	2.037(8)	2.093	2.046(7)	2.093	2.045(5)	2.093	2.040(3)	2.093	2.052(3)	2.059(4)	2.102
Pd2–Cl1	2.307(2)	2.343	2.303(2)	2.343	2.289 (2)	2.344	2.309(1)	2.343	2.3091(9)	2.2983(2)	2.332
C2–Pd1–N1	79.3(3)	79.0	79.0(3)	79.0	79.3(2)	79.1	79.6(2)	79.2	78.4(1)	78.5(2)	78.2
N1–Pd1–Cl1/N6	97.1(2)	95.6	96.8(2)	95.5	98.0 (1)	95.5	95.0(1)	95.0	102.9(1)	102.0(2)	104.9
Cl1/N6–Pd1–Cl2/N5	89.92(8)	90.9	90.09(8)	90.8	89.34(6)	90.8	90.75(4)	91.2	78.4(1)	78.4 (2)	77.3
Cl2/N5–Pd1–C2	93.6(3)	94.8	94.1(2)	94.8	93.3(2)	94.7	94.1(2)	94.9	102.9 (1)	104.3(2)	102.6
N1–Pd1–Cl2/N5	172.6(2)	173.1	172.8(2)	173.2	171.7(23)	173.3	172.6(1)	173.3	170.4(1)	170.7 (1)	170.2
C2–Pd1–Cl1/N6	175.7(3)	172.6	175.7(2)	172.5	177.4(2)	172.6	171.1(1)	171.4	164.5(4)	160.2(2)	162.6
C8–Pd2–N4	94.4(3)	98.0	95.2(3)	98.0	96.0(2)	97.8	95.2(2)	98.1	94.4(1)	98.4(2)	95.9
N4–Pd2–N3	79.4(3)	78.1	79.0(3)	78.1	79.8(2)	78.0	79.7 (1)	78.2	79.2(1)	79.0(2)	77.9
N3–Pd2–Cl1	98.9(2)	97.3	99.0(2)	97.3	96.9(1)	97.4	97.84(1)	97.0	96.2(8)	95.0 (1)	95.3
Cl1–Pd2–C8	87.3(3)	86.6	87.0(3)	86.6	87.3 (2)	86.8	87.4(1)	86.7	91.2(1)	88.3(1)	90.8
N4–Pd2–Cl1	176.8(2)	175.3	177.2(2)	175.3	175.7(1)	175.3	177.4(1)	174.8	172.40(9)	170.5 (0)	173.0
N3–Pd2–C8	173.7(4)	175.7	171.8(3)	175.7	175.7(2)	175.4	173.7(1)	176.0	169.1(1)	173.8(2)	173.1

Table S8 The calculated atomic coordinates for **1a** in the gas phase.

	x / Å	y / Å	z / Å		x / Å	y / Å	z / Å
Pd	1.6691	-0.6910	-0.6137	C	-2.6075	-3.8035	-0.7759
Pd	-1.2245	0.4091	-0.7151	H	-2.3699	-4.6971	-1.3416
Cl	0.0586	-0.2316	-2.5684	C	-3.7747	-2.6492	0.9809
N	2.6212	1.5546	0.9380	H	-4.4756	-2.6576	1.8068
N	-2.4612	0.8373	0.9177	C	3.7311	-1.9361	1.2895
N	1.7698	1.2803	0.0329	H	3.5277	-2.9183	0.8780
N	-2.2189	-1.4757	-0.4059	C	4.2941	0.6033	2.3770
C	-3.2498	-0.1901	1.3400	H	4.4855	1.5964	2.7718
C	-3.0968	-1.4803	0.6247	C	4.6979	-1.7723	2.2909
C	3.0261	-0.8315	0.8124	H	5.2383	-2.6446	2.6506
C	-1.9666	-2.6032	-1.0825	C	4.9839	-0.5128	2.8344
H	-1.2185	-2.5296	-1.8645	H	5.7393	-0.4101	3.6074
C	-4.2056	1.2200	3.0524	C	1.0111	2.3866	-0.4618
H	-4.8902	1.3630	3.8825	C	-0.3266	2.1898	-0.8582
C	3.3238	0.4424	1.3729	C	1.6106	3.6554	-0.5404
C	-2.5287	2.0239	1.5452	H	2.6421	3.7655	-0.2254
H	-1.8750	2.7966	1.1588	C	-1.0347	3.2999	-1.3417
C	-3.3848	2.2573	2.6165	H	-2.0628	3.1764	-1.6726
H	-3.3998	3.2332	3.0887	C	0.8873	4.7386	-1.0260
C	-4.1352	-0.0110	2.4078	H	1.3593	5.7137	-1.1010
H	-4.7663	-0.8280	2.7343	C	-0.4391	4.5619	-1.4294
C	-3.5283	-3.8216	0.2673	H	-1.0064	5.4002	-1.8251
H	-4.0439	-4.7383	0.5359	Cl	1.6451	-2.9821	-1.0854

Table S9 The calculated atomic coordinates for **2a**-alpha in the gas phase.

	x / Å	y / Å	z / Å
Pd	1.5412	-0.2760	-0.8474
Pd	-1.4966	0.2956	-0.6387
Cl	-0.2915	0.0301	-2.6305
N	2.2272	1.9856	0.8183
N	-2.6403	0.3775	1.1121
N	1.3566	1.6300	-0.0406
N	-2.1215	-1.7541	-0.4202
C	-3.2010	-0.8015	1.5010
C	-2.8919	-1.9890	0.6680
C	3.0260	-0.2737	0.4538
C	-1.7396	-2.7670	-1.2081
H	-1.0865	-2.5054	-2.0338
C	-4.2314	0.2890	3.3941
H	-4.8554	0.2478	4.2812
C	3.1455	0.9908	1.0988
C	-2.8551	1.4847	1.8429
H	-2.3797	2.3871	1.4776
C	-3.6417	1.4844	2.9903
H	-3.7825	2.4054	3.5447
C	-4.0075	-0.8602	2.6422
H	-4.4585	-1.7977	2.9424
C	-2.9445	-4.3380	0.1432
H	-3.2694	-5.3488	0.3692
C	-2.1355	-4.0812	-0.9595
H	-1.7985	-4.8752	-1.6160
C	-3.3250	-3.2826	0.9714
H	-3.9388	-3.4750	1.8429
C	3.9515	-1.2613	0.7720
H	3.8814	-2.2290	0.2858
C	4.1647	1.2414	2.0314
H	4.2257	2.2194	2.4992
C	4.9781	-1.0220	1.7072
C	5.0752	0.2355	2.3277
H	5.8714	0.4193	3.0439
C	0.3786	2.6160	-0.3785
C	-0.9348	2.2137	-0.6922
C	0.7404	3.9742	-0.3890
H	1.7609	4.2438	-0.1413
C	-1.8630	3.2112	-1.0249
H	-2.8791	2.9299	-1.2902
C	-0.1984	4.9433	-0.7235
H	0.0900	5.9900	-0.7462
C	-1.5042	4.5625	-1.0441
H	-2.2399	5.3125	-1.3227
Cl	1.8678	-2.4963	-1.5144
C	5.9544	-2.1232	2.0435
H	5.4736	-2.9017	2.6490
H	6.3280	-2.6104	1.1369
H	6.8114	-1.7447	2.6078

Table S10. The calculated atomic coordinates for **2a**-beta in the gas phase.

	x / Å	y / Å	z / Å
Pd	1.8008	-0.4783	-0.6631
Pd	-1.2375	0.1166	-0.6195
Cl	0.0800	-0.1027	-2.5444
N	2.4132	1.7289	1.1013
N	-2.4767	0.1579	1.0665
N	1.5878	1.4050	0.1882
N	-1.8882	-1.9332	-0.4962
C	-3.0629	-1.0279	1.3918
C	-2.7159	-2.1936	0.5430
C	3.2083	-0.5289	0.7194
C	-1.4703	-2.9262	-1.2911
H	-0.7735	-2.6457	-2.0738
C	-4.1869	0.0158	3.2577
H	-4.8570	-0.0463	4.1093
C	3.3076	0.7146	1.4045
C	-2.7250	1.2458	1.8155
H	-2.2269	2.1550	1.5008
C	-3.5714	1.2184	2.9191
H	-3.7371	2.1244	3.4911
C	-3.9290	-1.1133	2.4868
H	-4.3993	-2.0561	2.7364
C	-2.7521	-4.5266	-0.0498
H	-3.0930	-5.5413	0.1304
C	-1.8850	-4.2443	-1.1009
H	-1.5175	-5.0217	-1.7608
C	-3.1706	-3.4924	0.7866
H	-3.8302	-3.7052	1.6190
C	4.1041	-1.5398	1.0660
H	4.0538	-2.4958	0.5573
C	4.2718	0.9364	2.4026
H	4.3084	1.9031	2.8955
C	5.0640	-1.3156	2.0625
C	5.1539	-0.0865	2.7292
H	5.9078	0.0654	3.4956
C	0.6384	2.4066	-0.1772
C	-0.6558	2.0292	-0.5834
C	0.9997	3.7636	-0.1192
H	2.0013	4.0241	0.2043
C	-1.5553	3.0442	-0.9366
H	-2.5562	2.7748	-1.2675
C	0.0875	4.7456	-0.4800
H	0.3844	5.7907	-0.4466
C	-1.2062	4.4028	-0.9025
Cl	2.1504	-2.6787	-1.3780
C	-2.1814	5.4655	-1.3489
H	-2.0889	6.3741	-0.7451
H	-1.9999	5.7515	-2.3925
H	-3.2159	5.1153	-1.2833
H	5.7546	-2.1150	2.3198

Table S11. The calculated atomic coordinates for **3a**-alpha in the gas phase.

	x / Å	y / Å	z / Å
Pd	1.5488	-0.2956	-0.8378
Pd	-1.4901	0.2936	-0.6485
Cl	-0.2711	0.0007	-2.6287
N	2.2341	1.9713	0.8213
N	-2.6470	0.3997	1.0928
N	1.3594	1.6158	-0.0421
N	-2.1220	-1.7540	-0.4066
C	-3.2144	-0.7723	1.4926
C	-2.9018	-1.9720	0.6782
C	3.0227	-0.2901	0.4735
C	-1.7354	-2.7788	-1.1767
H	-1.0743	-2.5299	-2.0001
C	-4.2565	0.3458	3.3631
H	-4.8877	0.3180	4.2455
C	3.1397	0.9849	1.1116
C	-2.8636	1.5169	1.8076
H	-2.3822	2.4126	1.4338
C	-3.6594	1.5338	2.9486
H	-3.8014	2.4623	3.4900
C	-4.0303	-0.8138	2.6280
H	-4.4867	-1.7460	2.9366
C	-2.9556	-4.3280	0.1859
H	-3.2849	-5.3348	0.4231
C	-2.1363	-4.0885	-0.9132
H	-1.7954	-4.8924	-1.5555
C	-3.3406	-3.2604	0.9960
H	-3.9622	-3.4392	1.8648
C	3.9336	-1.2794	0.7950
H	3.8612	-2.2524	0.3186
C	4.1614	1.2293	2.0496
H	4.2253	2.2083	2.5149
C	4.9643	-1.0325	1.7343
C	5.0685	0.2337	2.3582
H	5.8608	0.4128	3.0800
C	0.3910	2.6041	-0.3905
C	-0.9223	2.2093	-0.7156
C	0.7546	3.9620	-0.4030
H	1.7731	4.2301	-0.1454
C	-1.8435	3.2067	-1.0655
H	-2.8572	2.9264	-1.3414
C	-0.1784	4.9335	-0.7489
H	0.1141	5.9793	-0.7698
C	-1.4815	4.5575	-1.0845
H	-2.2117	5.3091	-1.3732
Cl	1.8856	-2.5239	-1.4991
N	5.8398	-2.0437	2.0689
H	5.8988	-2.8277	1.4360
H	6.7160	-1.7836	2.4960

Table S12. The calculated atomic coordinates for **3a**-beta in the gas phase.

	x / Å	y / Å	z / Å
Pd	1.7755	-0.4992	-0.6522
Pd	-1.2409	0.1320	-0.6330
Cl	0.0648	-0.1087	-2.5608
N	2.4424	1.7157	1.0854
N	-2.4688	0.1974	1.0610
N	1.5926	1.3935	0.1922
N	-1.9093	-1.9099	-0.4898
C	-3.0584	-0.9819	1.4029
C	-2.7274	-2.1567	0.5604
C	3.1935	-0.5614	0.7188
C	-1.5055	-2.9119	-1.2806
H	-0.8145	-2.6422	-2.0720
C	-4.1565	0.0850	3.2711
H	-4.8176	0.0343	4.1304
C	3.3247	0.6889	1.3852
C	-2.7029	1.2937	1.8025
H	-2.2037	2.1974	1.4737
C	-3.5378	1.2809	2.9151
H	-3.6924	2.1932	3.4803
C	-3.9132	-1.0526	2.5077
H	-4.3861	-1.9905	2.7709
C	-2.7835	-4.4943	-0.0124
H	-3.1281	-5.5055	0.1800
C	-1.9261	-4.2258	-1.0751
H	-1.5696	-5.0110	-1.7318
C	-3.1870	-3.4506	0.8197
H	-3.8386	-3.6526	1.6611
C	4.0739	-1.5854	1.0648
H	3.9983	-2.5458	0.5677
C	4.3078	0.9028	2.3658
H	4.3713	1.8748	2.8455
C	5.0517	-1.3691	2.0461
H	5.7292	-2.1792	2.3049
C	5.1742	-0.1337	2.6943
H	5.9412	0.0140	3.4486
C	0.6581	2.3983	-0.1764
C	-0.6370	2.0373	-0.6060
C	1.0199	3.7566	-0.1049
H	2.0190	4.0107	0.2307
C	-1.5269	3.0504	-0.9675
H	-2.5251	2.7923	-1.3155
C	0.1283	4.7499	-0.4719
H	0.4294	5.7936	-0.4309
C	-1.1637	4.4110	-0.9192
Cl	2.0950	-2.7070	-1.3670
N	-2.0801	5.4009	-1.2600
H	-2.8158	5.1116	-1.8901
H	-1.6797	6.2903	-1.5251

Table S13. The calculated atomic coordinates for **4a**-alpha in the gas phase.

	x / Å	y / Å	z / Å		x / Å	y / Å	z / Å
Pd	-1.4022	-0.2175	-1.0220	H	-4.4630	0.5031	-0.3875
Pd	1.5330	0.6641	-0.4586	C	-3.4755	-2.6516	1.6721
Cl	0.5969	0.2304	-2.5621	H	-3.1705	-3.5303	2.2323
N	-1.2562	-2.4802	0.7750	C	-5.1581	-1.0202	1.0168
N	2.3951	1.2313	1.3628	C	-4.7652	-2.1738	1.7597
N	-0.5017	-1.7921	-0.0073	H	-5.4761	-2.6860	2.3949
N	1.1800	2.7838	-0.4459	C	0.8411	-2.2410	-0.1158
C	2.3580	2.5658	1.6345	C	1.8767	-1.3031	-0.3325
C	1.6600	3.4235	0.6467	C	1.1275	-3.6158	0.0004
C	-2.9025	-0.8465	0.0936	H	0.3089	-4.3056	0.1676
C	0.4883	3.4579	-1.3734	C	3.1856	-1.7810	-0.4362
H	0.0997	2.8688	-2.1972	H	4.0187	-1.1108	-0.6125
C	3.5597	2.2014	3.6979	C	2.4307	-4.0775	-0.1014
H	4.0162	2.5872	4.6038	H	2.6712	-5.1302	-0.0251
C	-2.5310	-2.0086	0.8444	C	3.4486	-3.1480	-0.3170
C	2.9864	0.3967	2.2343	Cl	-2.5845	1.5872	-1.9483
H	2.9824	-0.6507	1.9593	N	-6.4399	-0.5409	1.0953
C	3.5790	0.8386	3.4127	C	-7.4264	-1.2037	1.9359
H	4.0447	0.1224	4.0801	H	-7.1187	-1.2155	2.9893
C	2.9433	3.0684	2.8008	H	-8.3728	-0.6671	1.8687
H	2.9204	4.1312	3.0068	H	-7.6013	-2.2405	1.6201
C	0.7632	5.5070	-0.1602	C	-6.8402	0.6216	0.3096
H	0.6033	6.5742	-0.0433	H	-6.2572	1.5104	0.5788
C	0.2597	4.8297	-1.2666	H	-6.7121	0.4460	-0.7650
H	-0.3112	5.3384	-2.0349	H	-7.8927	0.8335	0.4987
C	1.4676	4.7977	0.8119	N	4.8341	-3.6170	-0.4136
H	1.8483	5.3125	1.6856	O	5.0363	-4.8310	-0.3453
C	-4.1951	-0.3720	0.1882	O	5.7223	-2.7715	-0.5467

Table S14. The calculated atomic coordinates for **4a**-beta in the gas phase.

	x / Å	y / Å	z / Å		x / Å	y / Å	z / Å
Pd	-1.3840	-0.3462	-1.0263	H	-4.5625	0.1966	-0.4167
Pd	1.4048	0.7931	-0.4608	C	-3.3452	-2.8761	1.6638
Cl	0.5997	0.2142	-2.5808	H	-2.9851	-3.7289	2.2298
N	-1.1147	-2.5514	0.8294	C	-5.0660	-1.3628	0.9826
N	2.0785	1.4638	1.4049	C	-4.6703	-2.4731	1.7348
N	-0.3999	-1.8130	0.0716	H	-5.3966	-2.9859	2.3514
N	0.8245	2.8657	-0.4980	C	0.9742	-2.1348	-0.0042
C	1.8467	2.7792	1.6724	C	1.9282	-1.1282	-0.2730
C	1.1292	3.5511	0.6292	C	1.4044	-3.4613	0.1969
C	-2.8631	-1.0444	0.0757	H	0.6600	-4.2223	0.4024
C	0.1295	3.4554	-1.4787	C	3.2749	-1.4806	-0.3510
H	-0.1152	2.8285	-2.3293	H	3.9969	-0.7062	-0.5802
C	2.9019	2.5467	3.8328	C	2.7394	-3.8034	0.1072
H	3.2215	2.9761	4.7769	H	3.0198	-4.8415	0.2310
C	-2.4483	-2.1662	0.8467	C	3.7205	-2.8166	-0.1735
C	2.6959	0.7007	2.3229	Cl	-2.6867	1.2870	-2.0643
H	2.8491	-0.3350	2.0443	N	5.0576	-3.1452	-0.2713
C	3.1220	1.2010	3.5489	C	6.0123	-2.1563	-0.7490
H	3.6133	0.5423	4.2563	H	5.7748	-1.7992	-1.7614
C	2.2600	3.3387	2.8860	H	6.0500	-1.2857	-0.0834
H	2.0803	4.3865	3.0914	H	7.0081	-2.6005	-0.7674
C	0.0419	5.5111	-0.2496	C	5.4649	-4.5422	-0.2319
H	-0.2642	6.5473	-0.1460	H	6.5528	-4.5985	-0.2842
C	-0.2797	4.7860	-1.3928	H	5.1538	-5.0180	0.7048
H	-0.8495	5.2246	-2.2040	H	5.0498	-5.1266	-1.0660
C	0.7509	4.8881	0.7770	N	-6.4713	-0.9294	1.0740
H	0.9890	5.4385	1.6790	O	-6.8120	0.0633	0.4329
C	-4.1962	-0.6472	0.1532	O	-7.2269	-1.5873	1.7935

Table S15. The calculated atomic coordinates for **3b**-alpha in the gas phase.

	x / Å	y / Å	z / Å		x / Å	y / Å	z / Å
C	-0.3200	-0.8703	-2.3854	H	-4.8989	1.0614	-2.9875
C	-0.0687	-1.1735	-3.7328	C	-3.5621	0.1383	-1.5868
H	0.4325	-0.4403	-4.3580	H	-2.9033	-0.2774	-2.3380
C	-0.4528	-2.4122	-4.2423	C	2.7456	1.7064	2.1584
H	-0.2592	-2.6547	-5.2827	H	2.0381	2.4959	1.9423
C	-1.0797	-3.3365	-3.4014	C	3.4727	1.6943	3.3433
H	-1.3715	-4.3099	-3.7859	H	3.3406	2.4929	4.0645
C	-1.3386	-3.0147	-2.0652	C	4.3513	0.6380	3.5734
H	-1.8309	-3.7456	-1.4308	H	4.9366	0.5893	4.4859
C	-0.9774	-1.7689	-1.5255	C	4.4493	-0.3737	2.6239
C	0.0961	2.5960	-1.8153	H	5.0923	-1.2253	2.8063
C	1.1075	2.5086	-0.8076	C	3.6881	-0.3068	1.4522
C	1.6838	3.6888	-0.3753	C	3.6777	-1.3856	0.4402
H	2.4999	3.6899	0.3421	C	4.6074	-2.4284	0.4313
C	1.2491	4.9511	-0.8719	H	5.4146	-2.4564	1.1528
C	0.2090	5.0082	-1.8292	C	4.4977	-3.4322	-0.5283
H	-0.1252	5.9717	-2.2018	H	5.2118	-4.2490	-0.5483
C	-0.3526	3.8384	-2.3007	C	3.4610	-3.3668	-1.4535
H	-1.1248	3.8591	-3.0633	H	3.3278	-4.1288	-2.2129
C	-2.0568	-1.0810	3.4065	C	2.5772	-2.2905	-1.3936
H	-1.1651	-1.7009	3.4061	H	1.7546	-2.2033	-2.0917
C	-2.7111	-0.7011	4.5764	Cl	0.0935	-2.5748	1.2650
H	-2.3301	-1.0243	5.5388	N	0.1459	0.3910	-1.8763
C	-3.8547	0.0878	4.4737	N	-0.4068	1.4377	-2.3461
H	-4.3935	0.4024	5.3619	N	1.8144	6.1014	-0.3983
C	-4.3085	0.4675	3.2124	H	1.6332	6.9731	-0.8716
H	-5.2002	1.0754	3.1226	H	2.6783	6.0544	0.1189
C	-3.6062	0.0496	2.0772	N	-3.2315	-0.1140	-0.3089
C	-4.0148	0.3799	0.6907	N	-2.4926	-0.7117	2.1948
C	-5.1475	1.1447	0.3966	N	2.8640	0.7496	1.2213
H	-5.7669	1.5332	1.1951	N	2.6829	-1.3208	-0.4768
C	-5.4855	1.4034	-0.9288	Pd	1.6163	0.5958	-0.4648
H	-6.3658	1.9933	-1.1627	Pd	-1.5944	-1.2747	0.3167
		C	-4.6784	0.8904	-1.9399		

Table S16. The calculated atomic coordinates for **3b**-beta in the gas phase.

	x / Å	y / Å	z / Å		x / Å	y / Å	z / Å
C	-0.5715	2.2565	1.0237	C	-3.4402	0.5213	0.8389
C	-0.6220	3.4831	1.7141	H	-2.9712	1.4666	1.0798
H	-0.3637	3.5066	2.7682	C	2.4336	-2.9286	0.3116
C	-0.9657	4.6472	1.0499	H	1.6175	-3.2631	0.9383
H	-0.9706	5.5956	1.5795	C	3.2367	-3.8353	-0.3708
C	-1.2864	4.6060	-0.3264	H	3.0532	-4.8991	-0.2707
C	-1.2691	3.3594	-0.9942	C	4.2617	-3.3411	-1.1749
H	-1.5289	3.3325	-2.0488	H	4.9115	-4.0145	-1.7245
C	-0.9204	2.1759	-0.3463	C	4.4274	-1.9643	-1.2834
C	-0.2676	-0.3054	3.4425	H	5.1899	-1.5608	-1.9375
C	0.6560	-1.1214	2.7277	C	3.5848	-1.1023	-0.5735
C	1.1233	-2.2618	3.3773	C	3.6537	0.3701	-0.6986
H	1.8749	-2.8987	2.9226	C	4.7266	1.0337	-1.2990
C	0.6507	-2.6103	4.6548	H	5.5843	0.4825	-1.6647
C	-0.2811	-1.8131	5.3223	C	4.6937	2.4223	-1.4074
H	-0.6324	-2.0926	6.3101	H	5.5194	2.9534	-1.8698
C	-0.7403	-0.6459	4.7176	C	3.5898	3.1099	-0.9131
H	-1.4414	0.0158	5.2163	H	3.5151	4.1892	-0.9828
C	-1.1011	-1.9926	-3.2722	C	2.5607	2.3827	-0.3177
H	-0.2813	-1.4056	-3.6755	H	1.6787	2.8749	0.0726
C	-1.4878	-3.2182	-3.8100	Cl	0.4893	0.9339	-2.8097
H	-0.9616	-3.6225	-4.6676	N	-0.1768	1.0841	1.7228
C	-2.5567	-3.8945	-3.2261	N	-0.7230	0.8641	2.8487
H	-2.8874	-4.8520	-3.6159	N	-2.8710	-0.1839	-0.1531
C	-3.2071	-3.3246	-2.1338	N	-1.7250	-1.4483	-2.2186
H	-4.0422	-3.8405	-1.6767	N	2.6119	-1.5980	0.2369
C	-2.7730	-2.0872	-1.6466	N	2.5906	1.0493	-0.2078
C	-3.4161	-1.3796	-0.5138	Pd	1.2876	-0.1929	1.0654
C	-4.5410	-1.8798	0.1489	Pd	-1.2065	0.4282	-1.2936
H	-4.9695	-2.8302	-0.1432	N	-1.5654	5.7623	-1.0137
C	-5.1202	-1.1494	1.1825	H	-1.8141	6.5885	-0.4919
H	-5.9944	-1.5323	1.6991	H	-1.9868	5.6881	-1.9268
C	-4.5622	0.0767	1.5317	H	1.0255	-3.5128	5.1295
		H	-4.9779	0.6874	2.3251		

Table S17. Wavelengths (λ / nm), oscillatory strengths (f) and character of electronic transitions from the ground to 32 lowest excited states of **1a**-**4a**, calculated by TD-DFT in $CHCl_3$.

exc. state		**1a**	**2a**-alpha	**2a**-beta	**3a**	**4a**
1	λ	515.7	507.5	513.2	502.2	564.9
	f	0.01	0.02	0.02	0.05	0.54
		MMLCT	MML'CT	MML'CT	LL'CT	IL(π-π*)
2	λ	479.9	474.6	476.1	482.9	507.0
	f	0.01	0.02	0.02	0.13	0.02
		XMLCT MMLCT	XML'CT, MML'CT	XML'CT, MML'CT	IL(π-π*), LL'CT+MMLCT	MMLCT
3	λ	443.6	446.8	448.5	454.40	494.8
	f	0.02	0.02	0.02	0.10	0.00
		MML'CT, LL'CT	MML'CT, LL'CT	MML'CT, LL'CT	XMLCT, MML(L')CT	LL'CT
4	λ	410.2	409.1	412.9	440.1	464.9
	f	0.08	0.09	0.16	0.00	0.09
		XMLCT, MML(L')CT, LL'CT	XML'CT, LL'CT, MML'CT	XML'CT, MML'CT	MML(L')CT	XMLCT
5	λ	407.8	403.8	406.4	415.2	433.03
	f	0.03	0.03	0.03	0.00	0.06
		XMLCT, MMLCT	XML'CT, LL'CT	XML(L')CT, LMMCT	LMMCT, LL'CT	IL(π-π*)
6	λ	399.0	403.4	402.1	405.1	431.4
	f	0.01	0.03	0.00	0.22	0.01
		XML(L')CT, ML(L')CT, LMMCT	XML(L')CT, LL'CT	LL'CT, MML'CT	XML(L')CT, MMLCT	MML'CT
7	λ	395.6	397.6	397.3	393.5	422.6
	f	0.05	0.07	0.01	0.10	0.04
		XML(L')CT, ML(L')CT, LL'CT	XML(L')CT, MML'CT	XML(L')CT LMMCT	LL'CT, LMMCT, XML(L')CT	XMLCT
8	λ	394.0	394.3	395.1	390.2	413.6
	f	0.10	0.10	0.13	0.01	0.00
		XML(L')CT, ML(L')CT, LMMCT	XML(L')CT, MML'CT, LMMCT	XML(L')CT, LMMCT	XML(L')CT	XMLCT IL(π-π*)
9	λ	386.2	386.5	387.3	384.5	405.1
	f	0.01	0.01	0.01	0.08	0.02
		LMMCT	LL'CT, LMMCT MML'CT	LL'CT, MML'CT	MML'CT	XMLCT IL(π-π*)
10	λ	380.3	383.2	385.0	382.6	397.0
	f	0.06	0.06	0.05	0.02	0.01
		XML(L')CT, LL'CT, MML'CT, LMMCT	LL'CT, MML'CT	XML'CT, LL'CT, LMMCT	LL'CT, XML(L')CT	MML'CT
11	λ	379.9	379.2	379.3	378.0	392.9

	f	0.00	0.06	0.04	0.00	0.15
		XML'CT, LL'CT, LMMCT	LMMCT, XML(L')CT	XML(L')CT, LMMCT	LMMCT, XMMCT	MMLCT XMLCT
12	λ	368.9	371.6	370.7	371.5	386.9
	f	0.00	0.01	0.04	0.01	0.02
			MML'CT, LL'CT, XML'CT	IL(π-π*), LL'CT, XML'CT	XML(L')CT, LL'CT	XML'CT, MML'CT LL'CT
13	λ	368.2	366.8	370.2	369.4	384.0
	f	0.12	0.10	0.07	0.01	0.01
		IL(π-π*)	IL(π-π*), LL'CT	IL(π-π*), LL'CT, XML'CT	XML(L')CT, LL'CT	LL'CT, LMMCT, XML'CT
14	λ	364.5	360.7	362.7	368.4	379.0
	f	0.02	0.00	0.01	0.00	0.01
		MMLCT	MML(L')CT,	MML(L')CT	LL'CT	XMLCT
15	λ	357.6	359.0	359.7	364.1	373.8
	f	0.01	0.00	0.01	0.00	0.00
		LMMCT, XMMCT	XMMCT, LMMCT	LMMCT	XML(L')CT, LL'CT	XMLCT, MMLCT IL(π-π*)
16	λ	355.2	356.2	355.9	357.2	370.9
	f	0.00	0.00	0.00	0.01	0.01
		LMMCT	XMMCT, LMMCT	LMMCT	XML'CT, LL'CT	XML'CT, LL'CT MML'CT
17	λ	352.3	353.5	353.0	356.4	368.4
	f	0.00	0.00	0.02	0.00	0.01
		MMLCT, XMMCT	XML'CT	XML'CT, MML'CT	XML(L')CT, LL'CT MML'CT	XML'CT, LL'CT MML'CT
18	λ	351.51	351.2	352.6	352.4	365.9
	f	0.03	0.01	0.01	0.02	0.00
		XML(L')CT, MML(L')CT	MML'CT, XMMCT	MML(L')CT, XMMCT	XMLCT, MML'CT	XML'CT, LL'CT MML'CT
19	λ	349.2	348.9	349.8	347.7	365.3
	f	0.02	0.01	0.01	0.04	0.00
		XMLCT, a, MMLCT	LL'CT, ML'CT	MML'CT	XML(L')CT, MML'CT	XMLCT, LL'CT
20	λ	345.42	347.0	348.9	347.2	358.4
	f	0.00	0.01	0.02	0.00	0.03
		LL'CT, LMMCT	MML(L')CT	LL'CT	XML(L')CT, MML'CT, LL'CT	MMLCT, XMLCT
21	λ	344.1	344.9	345.29	346.3	355.9
	f	0.02	0.03	0.02	0.00	0.02
		LL'CT	MML(L')CT, XML'CT	XML'CT, MML'CT	XMLCT, XMMCT, LMMCT	XML'CT, a
22	λ	342.2	342.6	343.01	343.2	353.03
	f	0.03	0.02	0.01	0.01	0.01
		MML(L')CT, L'LCT, XML'CT	MML'CT, XMMCT	MML'CT	LMMCT, XMMCT	MML(L')CT, XML(L')CT
23	λ	338.0	337.5	338.8	340.0	350.9

	f	0.00	0.00	0.00	0.0	0.01
		MML(L')CT, L'LCT XML(L')CT, L(L')CT	MML'CT, LL'CT	MML'CT, LL'CT	MMLCT	XML'CT
24	λ	334.0	334.6	338.8	340.0	348.2
	f	0.01	0.00	0.01	0.0	0.01
		MMLCT, LL'CT	MML(L')CT, XML(L')CT	XML(L')CT MML(L')CT	MMLCT	XML'CT
25	λ	325.0	324.9	338.8	340.0	344.5
	f	0.00	0.00	0.00	0.0	0.01
		MMLCT, L'LCT L(L')MMCT	MML'CT, LL'CT, LMMCT	MML'CT, LMMCT	MML'CT, LL'CT	mixed
26	λ	322.8	323.9	325.0	334.0.	342.7
	f	0.00	0.00	0.00	0.00	0.04
		L'LCT, MMLCT	MML'CT, LL'CT	LMMCT	LMMCT, LL'CT	MML'CT, LL'CT, XML'CT
27	λ	322.2	320.5	321.8	331.8	342.00
	f	0.00	0.00	0.00	0.01	0.00
		MML'CT, XML'CT, LL'CT	XML(L')CT, L'LCT	MML(L')CT, XML(L')CT L'LCT	LL'CT, XML'CT, MML'CT	XML(L')CT
28	λ	316.0	317.6	318.2	326.0	340.8
	f	0.03	0.00	0.00	0.01	0.01
		mixed	mixed	mixed	MML(L')CT, LL'CT	XML(L')CT, MML(L')CT
29	λ	314.3	315.8	316.2	321.1	337.7
	f	0.01	0.02	0.03	0.01	0.01
		LMMCT, XMMCT	L'LCT, XMLCT	L'LCT, LL'CT XML'CT	L'MMCT, MML'CT	MML'CT, XML'CT LL'CT
30	λ	311.0	313.2	312.6	322.1	332.32
	f	0.01	0.02	0.00	0.00	0.00
		MML'CT, L'LCT, XML'CT	LMMCT, XML'CT XMMCT	LL'CT, XML'CT MML'CT	mixed	L'LCT
31	λ	308.1	313.0	312.1	322.1	330.5
	f	0.01	0.02	0.01	0.01	0.01
		LMMCT, XMMCT	LL'CT XML'CT	mixed	mixed	XMLCT, MMLCT,
32	λ	307.8	310.2	310.93	314.33	329.8
	f	0.00	0.02	0.02	0.00	0.0
		MML'CT, XML'CT,LL'CT	XML'CT, LL'CT, MML'CT	L'LCT, LL'CT XML'CT	MML'CT, XML'CT, LL'CT	XMLCT

Table S18. Calculated excited states for **1a** in $CHCl_3$.

			energy / eV	λ_{max} / nm	oscillator strength
Excited	State	01:	2.4044	515.66	0.0136
Excited	State	02:	2.5838	479.85	0.0146
Excited	State	03:	2.7952	443.57	0.0164
Excited	State	04:	3.0222	410.24	0.0805
Excited	State	05:	3.0402	407.81	0.0343
Excited	State	06:	3.1083	398.88	0.0081
Excited	State	07:	3.1342	395.58	0.0537
Excited	State	08:	3.1472	393.95	0.0966
Excited	State	09:	3.2102	386.22	0.0105
Excited	State	10:	3.2602	380.30	0.0625
Excited	State	11:	3.2642	379.84	0.0016
Excited	State	12:	3.3612	368.87	0.0086
Excited	State	13:	3.3674	368.19	0.1210
Excited	State	14:	3.4011	364.54	0.0247
Excited	State	15:	3.4671	357.61	0.0062
Excited	State	16:	3.4873	355.54	0.0014
Excited	State	17:	3.5193	352.30	0.0041
Excited	State	18:	3.5272	351.51	0.0260
Excited	State	19:	3.5505	349.20	0.0195
Excited	State	20:	3.5894	345.42	0.0009
Excited	State	21:	3.6036	344.05	0.0239
Excited	State	22:	3.6236	342.16	0.0289
Excited	State	23:	3.6683	337.99	0.0028
Excited	State	24:	3.7026	334.86	0.0060
Excited	State	25:	3.8202	324.55	0.0028
Excited	State	26:	3.8405	322.84	0.0007
Excited	State	27:	3.8478	322.22	0.0006
Excited	State	28:	3.9233	316.02	0.0262
Excited	State	29:	3.9448	314.30	0.0053
Excited	State	30:	3.9862	311.03	0.0079
Excited	State	31:	4.0238	308.13	0.0012
Excited	State	32:	4.0288	307.75	0.0001

Table S19. Calculated excited states for **2a-**alpha in $CHCl_3$.

			energy / eV	λ_{max} / nm	oscillator strength
Excited	State	01:	2.4433	507.45	0.0211
Excited	State	02:	2.6126	474.57	0.0248
Excited	State	03:	2.7753	446.75	0.0188
Excited	State	04:	3.0307	409.10	0.0904
Excited	State	05:	3.0702	403.83	0.0270
Excited	State	06:	3.0738	403.35	0.0342
Excited	State	07:	3.1187	397.55	0.0707
Excited	State	08:	3.1444	394.30	0.0991
Excited	State	09:	3.2077	386.52	0.0055
Excited	State	10:	3.2357	383.18	0.0559
Excited	State	11:	3.2700	379.16	0.0566
Excited	State	12:	3.3367	371.58	0.0074
Excited	State	13:	3.3802	366.80	0.0965
Excited	State	14:	3.4376	360.68	0.0043
Excited	State	15:	3.4540	358.96	0.0037
Excited	State	16:	3.4804	356.23	0.0026
Excited	State	17:	3.5076	353.48	0.0031
Excited	State	18:	3.5307	351.16	0.0108
Excited	State	19:	3.5621	348.06	0.0311
Excited	State	20:	3.5730	347.01	0.0074
Excited	State	21:	3.5943	344.94	0.0338
Excited	State	22:	3.6193	342.56	0.0156
Excited	State	23:	3.6736	337.50	0.0029
Excited	State	24:	3.7056	334.59	0.0063
Excited	State	25:	3.8165	324.86	0.0039
Excited	State	26:	3.8279	323.89	0.0009
Excited	State	27:	3.8686	320.49	0.0006
Excited	State	28:	3.9043	317.56	0.0058
Excited	State	29:	3.9260	315.81	0.0266
Excited	State	30:	3.9583	313.23	0.0039
Excited	State	31:	3.9617	312.95	0.0001
Excited	State	32:	3.9967	310.21	0.0188

Table S20. Calculated excited states for **2a-**beta in $CHCl_3$.

			energy / eV	λ_{max} / nm	oscillator strength
Excited	State	01:	2.4158	513.21	0.0228
Excited	State	02:	2.6043	476.07	0.0199
Excited	State	03:	2.7644	448.51	0.0162
Excited	State	04:	3.0027	412.91	0.1606
Excited	State	05:	3.0505	406.44	0.0321
Excited	State	06:	3.0834	402.10	0.0038
Excited	State	07:	3.1204	397.33	0.0086
Excited	State	08:	3.1371	395.22	0.1341
Excited	State	09:	3.2016	387.25	0.0061
Excited	State	10:	3.2208	384.95	0.0472
Excited	State	11:	3.2685	379.33	0.0391
Excited	State	12:	3.3446	370.69	0.0403
Excited	State	13:	3.3495	370.16	0.0665
Excited	State	14:	3.4187	362.66	0.0093
Excited	State	15:	3.4472	359.66	0.0036
Excited	State	16:	3.4838	355.89	0.0007
Excited	State	17:	3.5142	352.81	0.0176
Excited	State	18:	3.5167	352.56	0.0066
Excited	State	19:	3.5442	349.83	0.0100
Excited	State	20:	3.5539	348.87	0.0169
Excited	State	21:	3.5913	345.24	0.0228
Excited	State	22:	3.6146	343.01	0.0105
Excited	State	23:	3.6596	338.79	0.0024
Excited	State	24:	3.6848	336.47	0.0055
Excited	State	25:	3.7940	326.79	0.0006
Excited	State	26:	3.8156	324.94	0.0034
Excited	State	27:	3.8523	321.85	0.0004
Excited	State	28:	3.8961	318.23	0.0048
Excited	State	29:	3.9215	316.17	0.0252
Excited	State	30:	3.9667	312.56	0.0014
Excited	State	31:	3.9724	312.11	0.0065
Excited	State	32:	3.9876	310.93	0.0156

Table S21. Calculated excited states for **3a** in $CHCl_3$.

			energy / eV	λ_{max} / nm	oscillator strength
Excited	State	01:	2.4687	502.23	0.0545
Excited	State	02:	2.5674	482.91	0.1282
Excited	State	03:	2.7283	454.44	0.0951
Excited	State	04:	2.8171	440.11	0.0038
Excited	State	05:	2.9864	415.16	0.0035
Excited	State	06:	3.0608	405.07	0.2173
Excited	State	07:	3.1507	393.52	0.0923
Excited	State	08:	3.1779	390.15	0.0086
Excited	State	09:	3.2243	384.53	0.0775
Excited	State	10:	3.2406	382.60	0.0197
Excited	State	11:	3.2800	378.00	0.0043
Excited	State	12:	3.3371	371.53	0.0078
Excited	State	13:	3.3564	369.40	0.0124
Excited	State	14:	3.3651	368.44	0.0023
Excited	State	15:	3.4054	364.08	0.0007
Excited	State	16:	3.4710	357.20	0.0078
Excited	State	17:	3.4788	356.40	0.0072
Excited	State	18:	3.5180	352.42	0.0235
Excited	State	19:	3.5656	347.72	0.0465
Excited	State	20:	3.5711	347.18	0.0022
Excited	State	21:	3.5800	346.33	0.0041
Excited	State	22:	3.6125	343.21	0.0054
Excited	State	23:	3.6468	339.98	0.0040
Excited	State	24:	3.6793	336.98	0.0016
Excited	State	25:	3.7126	333.95	0.0055
Excited	State	26:	3.7188	333.40	0.0007
Excited	State	27:	3.7368	331.79	0.0123
Excited	State	28:	3.8025	326.06	0.0059
Excited	State	29:	3.8491	322.11	0.0070
Excited	State	30:	3.8616	321.07	0.0102
Excited	State	31:	3.8989	318.00	0.0119
Excited	State	32:	3.9444	314.33	0.0019

Table S22. Calculated excited states for **4a** in $CHCl_3$.

			energy / eV	λ_{max} / nm	oscillator strength
Excited	State	01:	2.1949	564.88	0.5408
Excited	State	02:	2.4457	506.95	0.0249
Excited	State	03:	2.5059	494.77	0.0029
Excited	State	04:	2.6670	464.89	0.0925
Excited	State	05:	2.8632	433.03	0.0646
Excited	State	06:	2.8741	431.39	0.0119
Excited	State	07:	2.9336	422.63	0.0421
Excited	State	08:	2.9980	413.55	0.0038
Excited	State	09:	3.0605	405.11	0.0249
Excited	State	10:	3.1227	397.04	0.0134
Excited	State	11:	3.1559	392.86	0.1468
Excited	State	12:	3.2050	386.85	0.0243
Excited	State	13:	3.2290	383.97	0.0075
Excited	State	14:	3.2717	378.95	0.0126
Excited	State	15:	3.3170	373.78	0.0014
Excited	State	16:	3.3432	370.85	0.0089
Excited	State	17:	3.3656	368.39	0.0116
Excited	State	18:	3.3882	365.93	0.0010
Excited	State	19:	3.3943	365.27	0.0005
Excited	State	20:	3.4597	358.37	0.0305
Excited	State	21:	3.4841	355.85	0.0189
Excited	State	22:	3.5120	353.03	0.0067
Excited	State	23:	3.5337	350.86	0.0120
Excited	State	24:	3.5607	348.20	0.0086
Excited	State	25:	3.5991	344.49	0.0110
Excited	State	26:	3.6184	342.65	0.0358
Excited	State	27:	3.6256	341.96	0.0042
Excited	State	28:	3.6385	340.76	0.0083
Excited	State	29:	3.6711	337.73	0.0050
Excited	State	30:	3.7309	332.32	0.0001
Excited	State	31:	3.7518	330.47	0.0095
Excited	State	32:	3.7593	329.81	0.0003

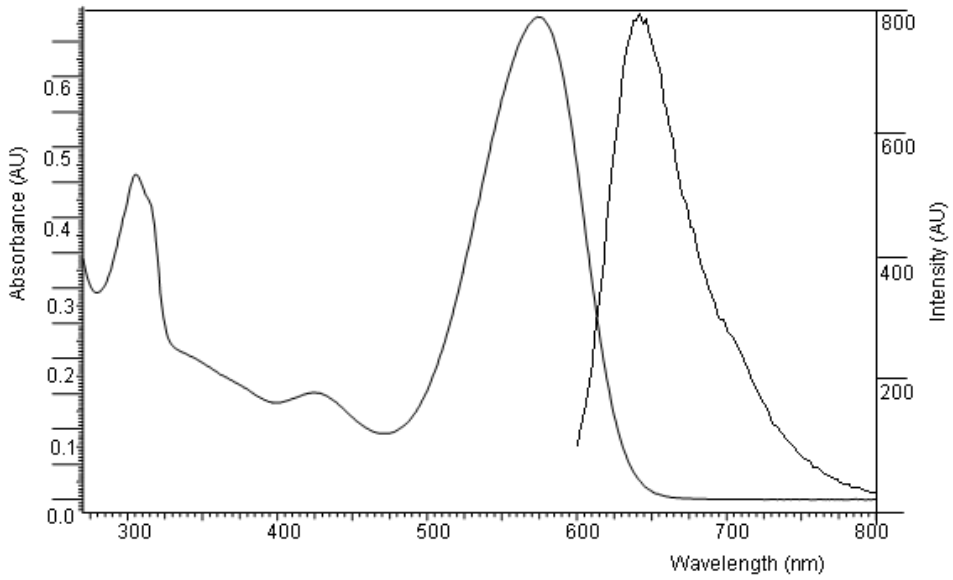


Fig. S9. Absorption and emission spectra of **4a** recorded in $CHCl_3$.

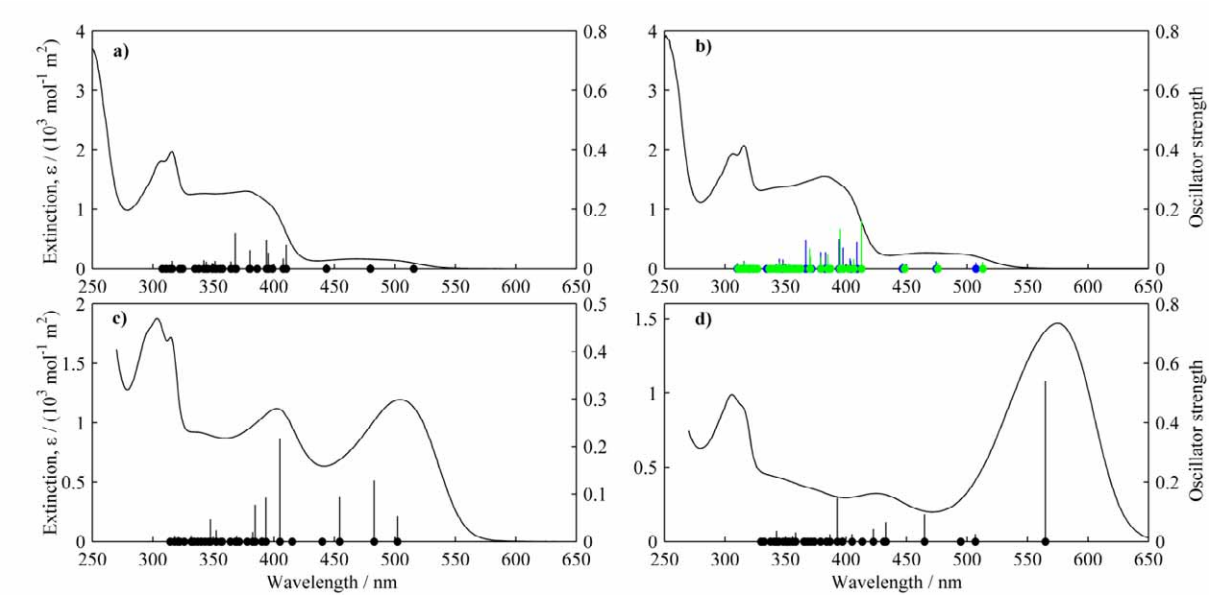


Fig. S10. UV-vis spectra of complexes **1a-4a**. a) **1a**; b) **2a**; c) **3a**; d) **4a**. Bold dots on the abscissa denote calculated transitions from the ground to excited singlet states; heights of vertical lines correspond to oscillator strengths. Blue dots and lines denote alpha isomer and the green ones denote beta isomer.

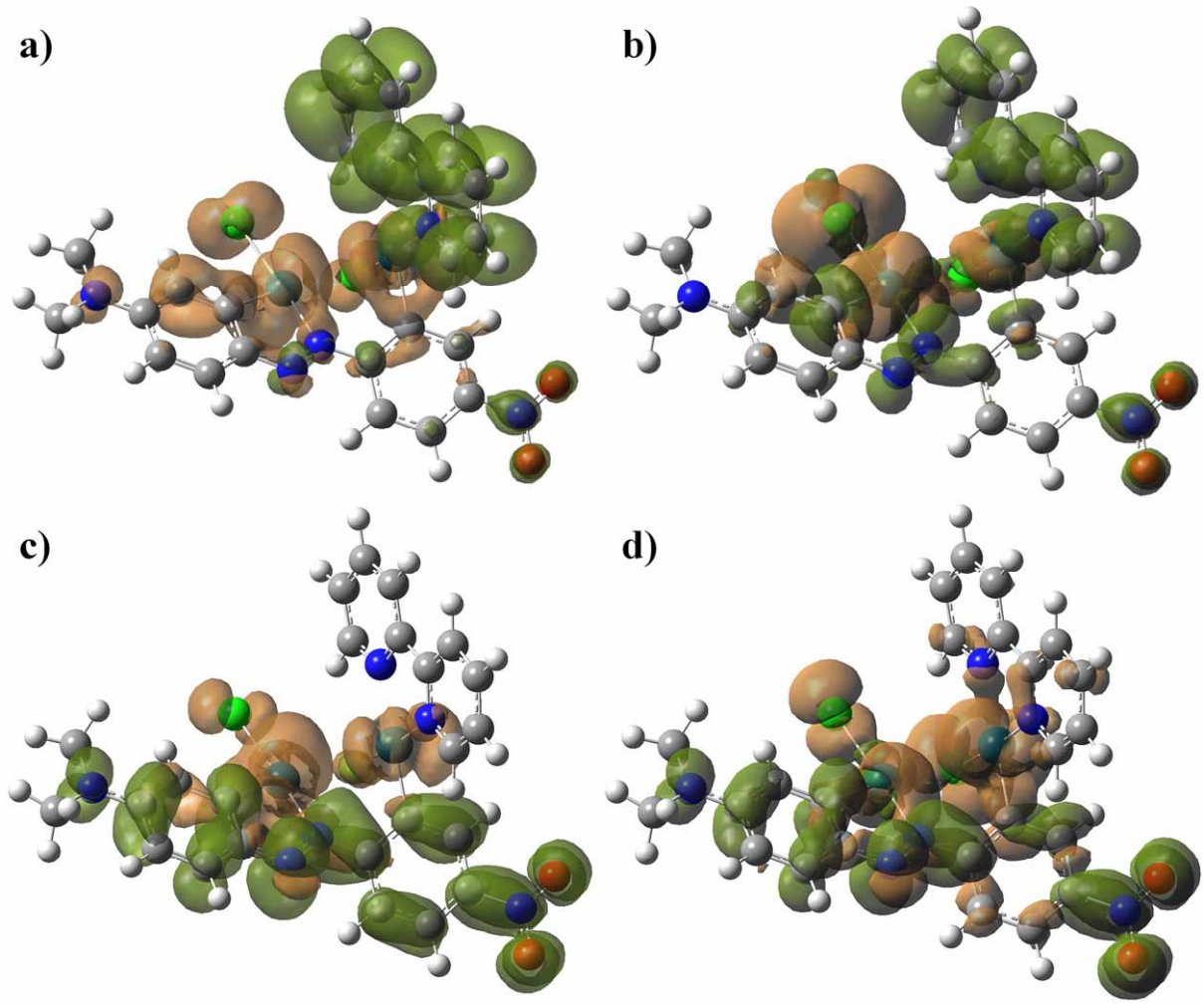
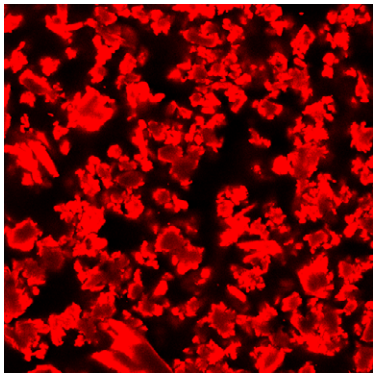
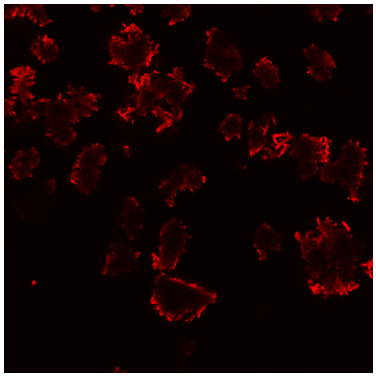


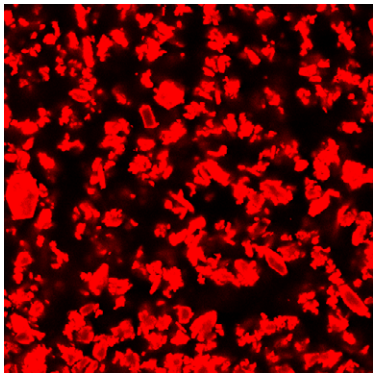
Fig. S11. Illustrative examples of charge density changes upon electronic excitation of **4a** from the ground state into a) 6th excited state, MML'CT, b) 21st excited state, XML'CT, c) 2nd excited state, MMLCT, d) 14th excited state, XMLCT. Isosurfaces in orange and green colours denote areas with increased and decreased electron density, respectively.



4a) λ_{exc}=633nm; λ_{em}=650-750nm



3a) λ_{exc} =514 nm; λ_{em}=570-630 nm



3b1) λ_{exc}=633nm; λ_{em}=640-730nm

Fig. S12. Solid-state fluorescence photographs of complexes **4a**, **3a** and **3b1**.