Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Synthesis and Electronic Structure of the first cyaphide-alkynyl complexes.

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General Experimental details.

All manipulations were performed under inert atmospheres (N_2 or Argon) using standard Schlenk-line and glove-box techniques. Solvents were dried by refluxing over molten alkali metals (hydrocarbons) or CaH_2 (chlorinated) and stored over potassium mirrors or 4 Å molecular sieves (CH_2Cl_2, $CHCl_3$, THF) in ampoules under argon. Reagents were obtained from standard commercial vendors; $Me_3SiC{\equiv}P$[S1] and $[Ru(dppe)_2Cl(C{\equiv}CC_6H_4OMe)]$ (**4**)[S2] were prepared by literature methods. NMR spectra were recorded on a VNMRS 400 MHz spectrometer: ^{1}H 399.5, ^{13}C 100.46, ^{29}Si 79.37, ^{31}P 161.71 MHz, reference to external Me_4Si, (^{1}H, ^{13}C, ^{29}Si) and 85 % H_3PO_4 (^{31}P) respectively. Carbon spectra were assigned with recourse to the 2D (HSQC, HMBC) spectra. UV/Vis spectra were recorded on a Thermo Spectronic UV300 instrument, IR spectra were recorded on a Perkin Elmer Spectrum One instrument. Raman spectra were recorded by Dr A. K. Brisdon, University of Manchester on a Nicolet Nexus FTIR/Raman. Mass spectra were recorded by Dr A. A. Sada of the departmental service and elemental analyses were obtained by Mr S. Boyer, London Metropolitan University Analytical Service.

Synthetic Procedures

$[RuCl(dppe)_2(C{\equiv}CCO_2Me)]$ (3)

$HCCCO_2Me$ (0.126 cm^3, 1.40 mmol) was added to a stirring solution of $[RuCl(dppe)_2][OTf]$ (0.760 g, 0.703 mmol) in DCM (10 cm^3) at ambient temperature. The solution was stirred for 16 h. then the solvent volume reduced to approx. 5 cm^3 under reduced pressure, with subsequent addition of a solution of KO^tBu (0.157 g, 1.40 mmol) in anal. grade MeOH (10 cm^3) at ambient temperature. A yellow/pink solution, with gradual formation of precipitate, was observed. After 1 h. the mixture was filtered and the pale yellow solid washed with anal. grade MeOH (3 x 5 mL), then dried *in vacuo*. Yield: 0.365 g, 0.360 mmol, 63%. Anal. Found: C, 65.96%; H, 4.95%. Calcd for $C_{56}H_{51}P_4O_2ClRu$: C, 66.17%; H, 5.02%. ν_{max}/cm^{-1} 2032 (CC). ^{1}H-NMR ($CDCl_3$, 30 °C, 399.5 MHz): δ_H 7.39-7.31 (16 H, m (br), C_6H_5), 7.23-7.19 (8 H, m (br), C_6H_5), 7.04-6.99 (16 H, m (br), C_6H_5), 3.51 (3 H, s, OCH_3), 2.69 (8 H, m, C_2H_4). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 30 °C, 150.81 MHz): δ_C 152.84 (s, *C*=O), 143.15 (s (br), Ru-*C*≡C), 135.79 (m, ipso-C_6H_5), 135.01 (m (br), C_6H_5), 134.50 (m (br), C_6H_5), 129.48 (d (J = 15.08), C_6H_5), 127.77 (m (br), C_6H_5), 127.53 (m (br), C_6H_5), 107.17 (s (br), Ru-C≡*C*), 51.25 (s, O*C*H_3), 30.91 (quint. ($^{1}J_{CP}$ = 11.79 Hz), C_2H_4). $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, 30 °C, 161.73 MHz): δ_P 48.09.

[Ru(dppe)$_2$(CCCO$_2$ Me)(P≡C(SiMe$_3$))][OTf] (5.OTf)

[RuCl(dppe)$_2$(CCCO$_2$Me)] (0.300 g, 0.295 mmol) and AgOTf (0.076 g, 0.295 mmol) were dissolved in DCM (5 cm^3) at ambient temperature with continual stirring, yielding a light purple suspension. The mixture was stirred for 10 min. before addition of TMSCP (6.80 cm^3, 0.043 M in toluene). The suspension was stirred for 1 h. and then filtered yielding an orange/red solution. Solvent was removed under reduced pressure, then the resulting mixture re-extracted with DCM, filtered and taken to dryness under reduced pressure to afford a copper coloured, powder. Yield: 0.224 g, 61%. ν_{max}/cm^{-1} 1265 (CP), 2098 (CC). Anal. Found: C, 58.59%; H, 4.75%. Calcd for $C_{61}H_{60}P_5O_5F_3SiSRu$: C, 58.79%; H, 4.82%. ^{1}H-NMR ($CDCl_3$, 30 °C, 399.5 MHz): δ_H 7.40 (12 H, m, C_6H_5), 7.33 (4 H, m, C_6H_5), 7.19 (8 H, m, C_6H_5), 7.10 (16 H, m, C_6H_5), 3.65 (3 H, s, CH_3), 2.82 (8 H, m, C_2H_4), −0.12 (9 H, s, Si(CH_3)$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 30 °C, 150.81 MHz): δ_C 192.59 (d ($^1J_{C\text{-}P}$ = 89.93 Hz), *C*≡P), 152.72 (s, *C*=O), 133.71 (m (br), C_6H_5), 132.90 (m (br), C_6H_5), 132.20 (dquint. (J = 209.41, 11.55 Hz), C_6H_5), 131.05 (d (J = 29.39 Hz), C_6H_5), 128.54 (m (br), C_6H_5), 128.31 (m (br), C_6H_5), 120.81 (m (br) Ru-*C*≡C), 108.77 (d (br) ($^3J_{CP}$ = 24.43 Hz), Ru-C≡*C*), 51.70 (s, *C*H$_3$), 29.87 (quint. ($^2J_{CP}$ = 11.84 Hz), C_2H_4), 0.33 (s, Si(*C*H$_3$)$_3$). ^{31}P{^{1}H}-NMR ($CDCl_3$, 30 °C, 161.73 MHz): δ_P 108.43 (quint. ($^2J_{PP}$ = 35.02 Hz), *P*≡C), 41.19 (d ($^2J_{PP}$ = 35.02 Hz), *P*Ph$_2$). ^{29}Si{^{1}H} NMR ($CDCl_3$, 298 K)δ_{Si}: −12.33.

[Ru(dppe)$_2$(CCC$_6$H$_4$OMe)(P≡C(SiMe$_3$))][OTf] (6.OTf)

[RuCl(dppe)$_2$(CCC$_6$H$_4$OMe)] (0.210 g, 0.198 mmol) and AgOTf (0.051 g, 0.198 mmol) were dissolved in DCM (5 cm^3) at ambient temperature with continual stirring, yielding a turquoise suspension. The mixture was stirred for 10 min. before addition of TMSCP (3.75 cm^3, 0.053 M in toluene). The suspension was stirred for 1 h. and then filtered yielding a green/brown solution. Solvent was removed under reduced pressure, then the resulting mixture re-extracted with DCM, filtered and taken to dryness under reduced pressure to afford a copper coloured, powder. Yield: 0.236 g, 92%. Anal. Found: C, 61.00%; H, 4.94%. Calcd for $C_{66}H_{64}P_5O_4F_3SiSRu$: C, 61.25%; H, 4.98%. ν_{max}/cm^{-1} 1265 (CP), 2040 (CC). ^{1}H-NMR ($CDCl_3$, 30 °C, 399.5 MHz): δ_H 7.67 (8 H, s(br), C_6H_5), 7.40 – 7.31 (8 H, *m*, C_6H_5), 7.18 – 7.05 (24 H, m, C_6H_5), 6.77 (4 H, m, *p*-C_6H_4), 3.83 (3 H, s, OCH_3), 2.84 (8 H, m, C_2H_4), −0.12 (9 H, s, Si(CH_3)$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 30 °C, 150.81 MHz): δ_C 188.2 (d, ($^1J_{CP}$ = 88.67), *C*≡P), 158.2 (s (br), C_6H_4), 133.6 (dquint. (J = 176.8, 11.10 Hz), *ipso*-C_6H_5), 133.5 (dquint. (J = 127.1, 2.3 Hz), C_6H_5), 131.2 (quintet, (J = 1.4 Hz), C_6H_4), 130.9 (s (br), C_6H_5), 128.4 (dquint. (J = 17.3, 2.3 Hz), C_6H_5), 119.6 (m (br), *ipso*-C_6H_4), 115.9 (d (br) ($^3J_{PP}$ = 23.0), Ru-C≡*C*), 113.4 (s (br) C_6H_4) 104.7 (d (br) ($^2J_{CP}$ = 83.6 Hz), Ru-*C*≡C), 55.4 (s, O*C*H$_3$), 30.8 (quint. ($^2J_{CP}$ = 11.6 Hz), C_2H_4), 0.51 (d, ($^2J_{CP}$ = 11.6 Hz), Si(CH_3)$_3$). ^{31}P{^{1}H}-NMR ($CDCl_3$, 30 °C, 161.73 MHz): δ_P 113.14 (quint. ($^2J_{PP}$ = 33.62Hz), *P*≡C), 41.18 (d ($^2J_{PP}$ = 33.62 Hz), PPh_2). ^{29}Si{^{1}H} NMR ($CDCl_3$, 298 K)δ_{Si}: −13.28.

Ru(dppe)$_2$(CCCO$_2$Me)(C≡P) (7)

[Ru(dppe)$_2$(TMSC≡P)(CCCO$_2$Me)][OTf] (0.190 g, 0.153 mmol) and KO^{t}Bu (0.017 g, 0.153 mmol) were dissolved in THF (5 cm^3) at ambient temperature with continual stirring. The solution was stirred for 1 h. before removal of solvent under reduced pressure, and the residue extracted with CH_2Cl_2. After filtration, the solvent was removed under reduced pressure to afford a beige solid. Yield: 0.094 g, 60 %. Anal. Found: C, 66.70%; H, 4.78%. Calcd for $C_{57}H_{51}P_5O_2Ru$: C, 66.86%; H, 5.02%. ν_{max}/cm^{-1} 1253 (CP), 2036 (CC). ^{1}H-NMR ($CDCl_3$, 30 °C, 399.5 MHz): δ_H 7.63 (6 H, m (br), C_6H_5), 7.38 (6 H, m (br), C_6H_5), 7.29 (6 H, t (J_{HH} = 7.51 Hz), C_6H_5), 7.22 (6 H, t (J_{HH} = 7.51 Hz), C_6H_5), 7.10 (8 H, t (J_{HH} = 7.51 Hz), C_6H_5), 7.01 (8 H, t (J_{HH} = 7.51 Hz), C_6H_5), 3.53 (3 H, s, CH_3), 2.86 (4 H, m (br), C_2H_4), 2.67 (4 H, m (br), C_2H_4). ^{13}C{^{1}H}-NMR ($CDCl_3$, 30 °C, 150.81 MHz): δ_C 279.12 (m (br), *C*≡P), 152.96 (s, *C*=O), 143.78 (m (br), Ru-*C*≡C), 136.46 (m (br), C_6H_5), 134.69 (m (br), C_6H_5), 135.07 (d (J = 36.98 Hz), C_6H_5), 127.74 (m (br), C_6H_5), 127.48 (m (br), C_6H_5), 112.42 (s, Ru-C≡*C*), 51.17 (s, O*C*H$_3$), 31.34 (quint. (J_{CP} = 11.95 Hz), C_2H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$, 30 °C, 161.73 MHz): δ_P 161.52 (s (br), *P*≡C), 52.73 (d (J_{PP} = 3.81 Hz), *P*Ph$_2$).

Ru(dppe)$_2$(C≡P)(CCC$_6$H$_4$OMe) (8)

[Ru(dppe)$_2$(TMSC≡P)(CCC$_6$H$_4$OMe)][OTf] (0.326 g, 0.252 mmol) and KO^{t}Bu (0.029 g, 0.258 mmol) were dissolved in THF (5 cm^3) at ambient temperature with continual stirring. The solution was stirred for 1 h. before removal of solvent under reduced pressure, and the residue extracted with CH_2Cl_2. After filtration, the solvent was removed under reduced pressure to afford a beige solid. Yield: 0.162 g, 60%. Anal. Found: C, 69.30%; H, 5.23%. Calcd for $C_{62}H_{55}P_5ORu$: C, 69.46%; H, 5.17%. ν_{max}/cm^{-1} 1261 (CP), 2032 (CC). ^{1}H-NMR (CD_2Cl_2, 30 °C, 399.5 MHz): δ_H 7.57 (16 H, dm (J = 27 Hz), C_6H_5), 7.23 (8 H, dt (J = 30.1, 7.4 Hz), C_6H_5), 7.03 (16 H, dt (J = 43.6, 7.5 Hz), C_6H_5), 6.69 (4H, s,(br), C_6H_4), 3.77 (3 H, s OCH_3), 2.89 (8 H, m (br), C_2H_4), 2.65 (8 H, m (br), C_2H_4).. ^{13}C{^{1}H}-NMR (CD_2Cl_2, 30 °C, 150.81 MHz): δ_C 281.9 (m (br), *C*≡P), 156.7 (s, *p*-C_6H_4), 135.51 (dquint. (J = 111.18, 10.26 Hz), *ipso*-C_6H_5), 135.4 (m (br), C_6H_5), 135.0 (m (br), C_6H_5) 131.4 (m (br), C_6H_4) 129.5 (d (J = 20 Hz), C_6H_5), 127.6 (m (br), C_6H_5), 127.4 (m (br), C_6H_5), 123.6 (s, Ru-*C*≡C), 119.0 (s, Ru-C≡*C*), 55.7 (s, CH_3), 31.7 (quint. (J_{CP} = 11.81 Hz), C_2H_4), (129.05 (d (J = 39.84 Hz), C_6H_5), 126.98 (dquint. (J = 27.25, 2.12 Hz), C_6H_5), 112.02, 59.13 (s, O*C*H$_2$), 30.72 14.50 (s, *C*H$_3$). ^{31}P{^{1}H}-NMR ($CDCl_3$, 30 °C, 161.73 MHz): δ_P 159.5 (m (br), *P*≡C), 50.8 (d ($^3J_{PP}$ = 3.4 Hz), *P*Ph$_2$).

Crystallography.

Diffraction data were obtained on either an Enraf Nonius Kappa CCD using Mo-Kα radiation (λ = 0.71073), or an Agilent Excalibur with CCD plate detector using Cu-Kα radiation (λ =1.54184) and solved using either SHELX-97[S3] or Olex 2.0.[S4]

Compound 3 (CCDC 962350): *Crystal Data*: $C_{56}H_{51}ClO_2P_4Ru$, M_w = 1101.29, monoclinic, *Cc* (no 9), *a* = 22.6782(6) Å, *b* = 13.3919(3) Å, *c* = 16.9067(4) Å, β = 102.139(1)°. *V* = 5019.8(2) Å^3. *Z* = 4. D_c 1.457 Mg m^{-3}, μ(Mo-Kα) = 0.643 mm^{-1}, *T* = 173(2) K, 11095 independent reflections, full-matrix F^2 refinement. R_1 = 0.053, wR_2 = 0.1184 on 8097 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 55°], 606 parameters.

Compound 5.OTF (CCDC 962351): *Crystal Data*: $C_{60}H_{60}O_2P_5RuSi$, M_w = 1246.16, monoclinic, *Cc* (no 9), *a* = 27.1458(6) Å, *b* = 12.4837(3) Å, *c* = 18.8950(5) Å, β = 102.193(2)°. *V* = 6258.7(3) Å^3. *Z* = 4. D_c 1.322 Mg m^{-3}, μ(Mo-Kα) = 0.485 mm^{-1}, *T* = 173(2) K, 13387 independent reflections, full-matrix F^2 refinement. R_1 = 0.077, wR_2 = 0.2030 on 8097 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 54°], 741 parameters.

Compound 8 (CCDC 990881): *Crystal Data*: $C_{62}H_{55}OP_5Ru$, M_w = 1071.98, triclinic, P -1 (no 2), *a* = 9.9951(7) Å, *b* = 11.9374(6) Å, *c* = 21.7684(13) Å, α = 85.981(5) °, β = 86.336(5), ° γ = 85.461(5) °. *V* = 2578.3(3) Å^3. *Z* = 2. D_c 1.381 Mg m^{-3}, μ(Cu-Kα) = 4.252 mm^{-1}, *T* = 173 K, 9644 independent reflections, full-matrix F^2 refinement. R_1 = 0.0458 wR_2 = 0.1365 on 7915 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 143.6°], 642 parameters.

Computational Details. Calculations were performed using Gaussian 09W, Revision C.01,[S5] running on either an Intel Core 2 Quad Q9550 or Intel Core i5-2500 (quad, 3.3 GHz), equipped with 4 GB RAM, results were visualised using GaussView 5.0; orbital contributions and UV/Vis spectra were calculated using GaussSum2.2.[S6] Geometries were optimised with the hybrid density functional B3LYP, using the RECP basis set Lanl2dz for Ru and 6-31G** for all other atoms. Minima were characterised by frequency calculations, and calculated frequencies adjusted by standard scaling factors. Excited states were calculated using TD-DFT with the B3LYP functional and 3-21G* basis set on all atoms; no solvent model was used.

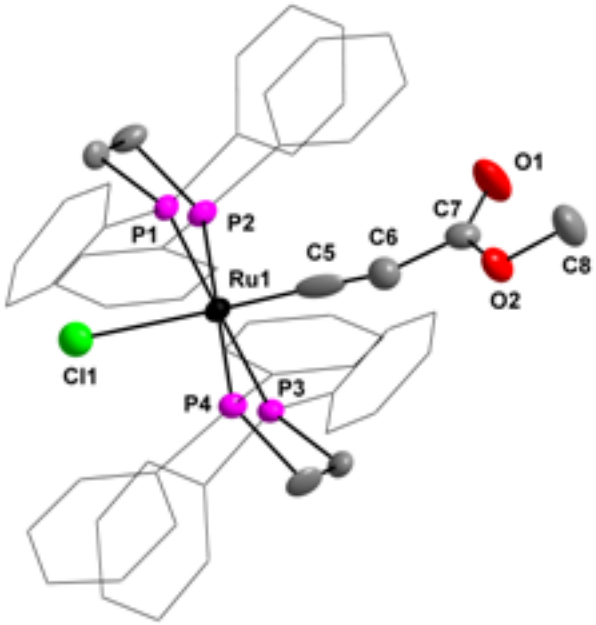

Figure S1: Molecular structure of **3** with hydrogen atoms omitted and phenyl rings reduced for clarity; 50 % thermal ellipsoids. Selected Bond distances (Å) and angles (deg.).: Ru(1)-Cl(1) 2.550(2), Ru(1)-C(5) 1.875(7), C(5)-C(6) 1.136(10), C(6)-C(7) 1.541(8), C(5)-Ru(1)-Cl(1) 177.8(2), C(6)-C(5)-Ru(1) 175.8(6), C(5)-C(6)-C(7) 165.6(7)

Table S1: Atomic coordinates for optimized structure of **7**.

	X	Y	Z		X	Y	Z		X	Y	Z		X	Y	Z
Ru	-0.02811	0.111538	-0.10181	**H**	1.296441	1.780416	3.735027	**C**	1.955298	5.252152	0.149798	**H**	1.154357	-3.40961	-0.33558
C	-0.15132	1.68234	-1.41253	**C**	-2.28334	2.718809	1.319624	**H**	0.376991	3.872847	0.58605	**C**	4.274159	-4.58371	-0.93448
C	0.215487	-1.48554	1.212843	**C**	-2.83151	3.108219	0.087796	**C**	3.331515	5.445477	0.023631	**H**	5.805877	-3.53023	-2.02907
C	0.407009	-2.43896	1.979628	**C**	-2.30591	3.637821	2.383292	**H**	5.273544	4.520518	0.176701	**H**	2.53696	-5.35951	0.103257
C	0.579792	-3.74512	2.541463	**C**	-3.39213	4.376024	-0.07338	**H**	1.266853	6.065982	-0.05773	**H**	4.895214	-5.45355	-0.73878
O	0.967252	-3.85239	3.84341	**H**	-2.81085	2.42507	-0.75011	**H**	3.723084	6.415084	-0.27079	**C**	-3.30305	-0.00927	-1.94016
C	1.193222	-2.66024	4.598577	**C**	-2.8551	4.910366	2.216771	**C**	3.042942	0.46124	2.090353	**C**	-3.40048	0.951475	-2.96025
H	1.946663	-2.02278	4.127224	**H**	-1.90533	3.370041	3.354974	**C**	3.767465	1.075836	3.129598	**C**	-4.4464	-0.29211	-1.17308
H	0.267171	-2.08958	4.727692	**C**	-3.40212	5.281978	0.987358	**C**	3.449777	-0.80408	1.653947	**C**	-4.60908	1.607689	-3.20535
H	1.550723	-2.99426	5.574507	**H**	-3.80934	4.654225	-1.03648	**C**	4.862003	0.438393	3.711187	**H**	-2.53415	1.209205	-3.55614
O	0.400218	-4.77972	1.912171	**H**	-2.85927	5.606755	3.050638	**H**	3.493635	2.068375	3.474756	**C**	-5.65004	0.369201	-1.41714
P	-0.19167	2.865294	-2.46442	**H**	-3.83132	6.271622	0.85824	**C**	4.551111	-1.44332	2.232773	**H**	-4.40324	-1.03936	-0.38843
P	1.53347	-0.88433	-1.76886	**C**	-3.13095	0.056642	2.017443	**H**	2.892949	-1.30865	0.878403	**C**	-5.73605	1.321125	-2.43457
P	-1.71789	-0.89313	-1.57755	**C**	-4.35685	0.694941	2.264931	**C**	5.257541	-0.82552	3.263004	**H**	-4.66373	2.344241	-4.00203
C	0.456611	-1.69174	-3.07109	**C**	-3.0463	-1.33373	2.200284	**H**	5.408698	0.930344	4.510885	**H**	-6.51951	0.135883	-0.80963
H	1.00866	-1.77178	-4.01223	**C**	-5.46811	-0.03917	2.684224	**H**	4.842481	-2.42622	1.874991	**H**	-6.67494	1.832694	-2.6271
H	0.292936	-2.71456	-2.71825	**H**	-4.45294	1.765215	2.125587	**H**	6.11068	-1.32201	3.716753	**C**	-2.32318	-2.64645	-1.44884
C	-0.88144	-0.97544	-3.24479	**C**	-4.15919	-2.06384	2.620267	**C**	2.620751	0.271695	-2.71031	**C**	-3.28173	-3.12917	-2.36056
H	-1.52302	-1.5044	-3.95652	**H**	-2.10992	-1.84519	2.013234	**C**	3.692705	0.880471	-2.03974	**C**	-1.78023	-3.53683	-0.51525
H	-0.73044	0.050273	-3.58841	**C**	-5.37446	-1.42004	2.861573	**C**	2.417752	0.581082	-4.06192	**C**	-3.67983	-4.46414	-2.3307
P	1.581456	1.313753	1.324549	**H**	-6.40832	0.473064	2.869396	**C**	4.547313	1.758238	-2.70459	**H**	-3.72733	-2.45901	-3.08962
P	-1.62012	1.000792	1.49548	**H**	-4.07304	-3.13864	2.751571	**H**	3.873081	0.655414	-0.99344	**C**	-2.17713	-4.87775	-0.48729
C	-0.64726	1.066678	3.080888	**H**	-6.24089	-1.99017	3.184971	**C**	3.268372	1.466176	-4.7267	**H**	-1.04661	-3.19179	0.199835
H	-1.24579	1.473449	3.902252	**C**	2.316267	2.935292	0.799729	**H**	1.58799	0.149836	-4.60986	**C**	-3.12775	-5.34329	-1.39308
H	-0.42162	0.023474	3.315382	**C**	3.696935	3.137909	0.655541	**C**	4.336981	2.054993	-4.05218	**H**	-4.42224	-4.81883	-3.04055
C	0.636827	1.867245	2.868096	**C**	1.451019	4.007642	0.525475	**H**	5.370847	2.217102	-2.16592	**H**	-1.72493	-5.53721	0.247084
H	0.408611	2.927873	2.738462	**C**	4.199907	4.38314	0.272704	**H**	3.08815	1.69795	-5.77246	**H**	-3.43947	-6.38408	-1.37463

Table S2: Atomic coordinates for optimized structure of **8**.

	X	Y	Z		X	Y	Z		X	Y	Z		X	Y	Z
Ru	0.658062	0.021785	0.130579	**H**	2.061743	1.69308	-4.37222	**C**	-0.51008	-2.86452	-1.95331	**C**	0.596941	-0.55127	-3.33124
P	0.63094	1.59672	1.994087	**C**	3.272699	-2.84495	-1.21477	**C**	2.944846	3.227984	2.340862	**H**	1.609237	-0.42969	-3.72593
P	0.795373	-1.56008	-1.74927	**H**	3.186414	-2.42865	-0.22129	**H**	3.45275	2.337051	2.687065	**H**	0.025705	-1.12953	-4.06355
P	0.743399	1.678214	-1.64377	**C**	-2.03533	-2.82488	1.365516	**C**	-0.04634	0.815615	-3.09348	**O**	-8.14624	0.136121	-1.61248
P	0.481238	-1.62552	1.950288	**H**	-1.93064	-2.38969	0.381444	**H**	-1.09382	0.710694	-2.80187	**C**	-5.87747	0.827425	-2.24127
P	4.252485	0.161885	0.630797	**C**	-0.8653	3.136092	3.863683	**H**	-0.00768	1.439406	-3.99252	**H**	-6.21078	1.383903	-3.10986
C	3.252715	2.914449	-1.42595	**H**	0.067951	3.648641	4.074135	**C**	0.707783	-0.68205	3.56962	**C**	4.378148	-3.636	-1.54304
H	3.003588	3.006665	-0.37679	**C**	2.438692	-3.09634	-3.46759	**H**	-0.29987	-0.50177	3.956113	**H**	5.128877	-3.83894	-0.78528
C	-3.16064	-3.60002	1.666955	**H**	1.679195	-2.91563	-4.22236	**H**	1.230946	-1.31457	4.292517	**C**	3.963954	-3.75453	2.711564
H	-3.90368	-3.77764	0.895213	**C**	-2.00683	3.477362	4.586871	**C**	-4.96462	-0.58388	-0.01312	**H**	4.953204	-3.53404	3.102401
C	4.463112	3.430282	-1.8874	**H**	-1.94778	4.24521	5.353479	**H**	-4.61466	-1.13654	0.852949	**C**	4.518656	-4.15019	-2.83012
H	5.134833	3.918396	-1.18759	**C**	2.294256	-2.56268	-2.17315	**C**	-2.23784	4.45674	-0.88561	**H**	5.380653	-4.76086	-3.08461
C	-2.13884	1.50477	2.616581	**C**	0.197641	4.418427	-2.24076	**H**	-3.18555	4.461015	-0.35458	**C**	-6.79144	0.161128	-1.41751
H	-2.19886	0.751165	1.83997	**H**	1.144907	4.422509	-2.76765	**C**	3.046137	5.58711	1.799381	**C**	-1.22867	-3.14483	3.619041
C	-1.41817	0.014299	-0.25043	**C**	-6.32118	-0.54405	-0.29948	**H**	3.604634	6.517298	1.743571	**H**	-0.47312	-2.999	4.384797
C	1.735165	-2.98459	2.110718	**H**	-7.04335	-1.05396	0.330733	**C**	1.707836	5.54535	1.403798	**C**	-3.32655	-4.13701	2.942364
C	2.683525	0.070992	0.412598	**C**	3.021784	-2.72873	2.611336	**H**	1.216607	6.440795	1.034542	**H**	-4.2033	-4.73522	3.174966
C	-2.61967	0.038295	-0.53218	**H**	3.304961	-1.72613	2.907234	**C**	-1.78458	-2.54678	-2.44916	**C**	3.543912	-3.87852	-3.79487
C	-1.05727	-2.58756	2.338044	**C**	4.816719	3.304714	-3.23154	**H**	-2.02758	-1.52664	-2.719	**H**	3.641605	-4.28043	-4.79962
C	2.362725	2.277354	-2.30525	**H**	5.764622	3.698394	-3.58754	**C**	3.659976	4.426125	2.269614	**C**	-2.49138	-4.85085	-2.21325
C	-1.47026	3.290416	-0.9059	**C**	1.420887	-4.29384	1.710325	**H**	4.700342	4.444815	2.581708	**H**	-3.25459	-5.61708	-2.31662
H	-1.82515	2.400539	-0.39912	**H**	0.429132	-4.52062	1.334366	**C**	3.945696	2.66766	-4.1151	**C**	2.365648	-5.31618	1.805943
C	-0.24114	3.256325	-1.58537	**C**	-0.57092	5.583945	-2.21424	**H**	4.207978	2.56511	-5.16442	**H**	2.100188	-6.32281	1.494913
C	-0.91801	2.147245	2.863331	**H**	-0.21128	6.473463	-2.72435	**C**	-0.24545	-4.19582	-1.59253	**C**	3.640577	-5.05054	2.308438
C	-3.28295	1.851305	3.342675	**C**	-4.01702	0.078621	-0.83016	**H**	0.736515	-4.47103	-1.22315	**H**	4.374343	-5.84766	2.388356
H	-4.22177	1.349068	3.127224	**C**	1.438601	0.646852	3.380915	**C**	-3.22139	2.836631	4.326376	**C**	-2.35602	-3.90583	3.921105
C	-1.79001	5.608312	-1.53573	**H**	2.475457	0.478341	3.083535	**H**	-4.11153	3.10686	4.887892	**H**	-2.47267	-4.32432	4.916958
H	-2.38621	6.516519	-1.51464	**H**	1.41922	1.238218	4.302276	**C**	-1.22806	-5.17883	-1.71889	**C**	-8.67158	0.835512	-2.72643
C	-4.51391	0.782081	-1.94452	**C**	1.597948	3.173595	1.945539	**H**	-1.00082	-6.20354	-1.43801	**H**	-9.7525	0.68698	-2.6962
H	-3.81657	1.312684	-2.586	**C**	0.990095	4.351857	1.477435	**C**	-2.76514	-3.53219	-2.57967	**H**	-8.28138	0.443054	-3.6751

C	2.726289	2.164029	-3.6566	**H**	-0.051	4.343878	1.175204	**H**	-3.74423	-3.26288	-2.96527	**H**	-8.455	1.910789	-2.67192

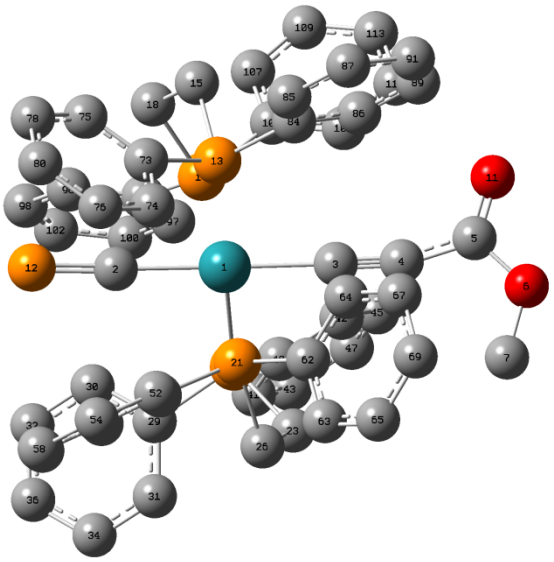

Figure S2: Optimised geometry of **7**. Selected geometric parammeters (Å, °). Ru(1)-C(2) 2.04953, Ru(1)-C(3) 2.08286, C(3)-C(4) 1.23841, C(4)-C(5) 1.43232, C(5)-O(6) 1.36261, C(5)-O(11) 1.22420, C(2)-P(12) 1.58350. Ru(1)-C(2)-P(12)177.32006, Ru(1)-C(3)-C(4) 177.72607, C(3)-C(4)-C(5) 164.49122. ν_{CP} 1238 cm^{-1}

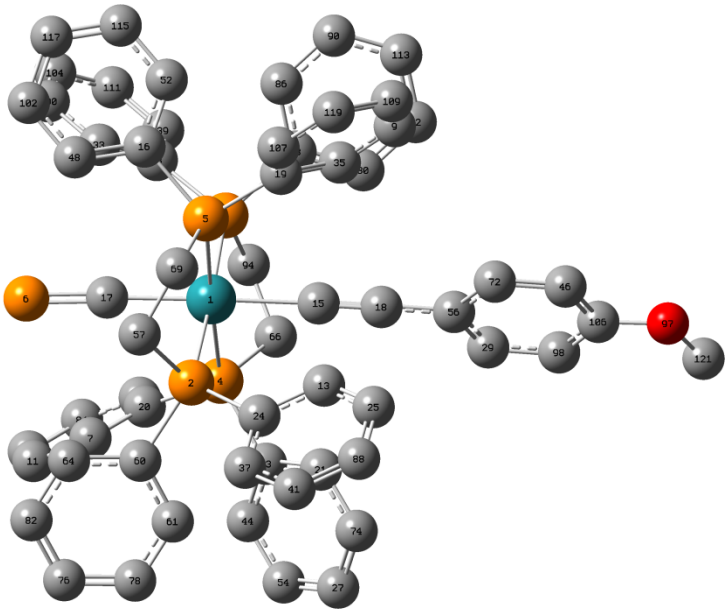

Figure S3: Optimised geometry of **8**. Selected geometric parammeters (Å, °). Ru(1)-C(17) 2.04559, Ru(1)-C(15) 2.11091, C(15)-C(18) 1.23433, C(18)-C(55) 1.42033, C(17)-P(6) 1.58667. Ru(1)-C(17)-P(6)178.09434, Ru(1)-C(15)-C(18) 176.90735, C(15)-C(18)-C(55) 178.73669. ν_{CP} 1224 cm^{-1}

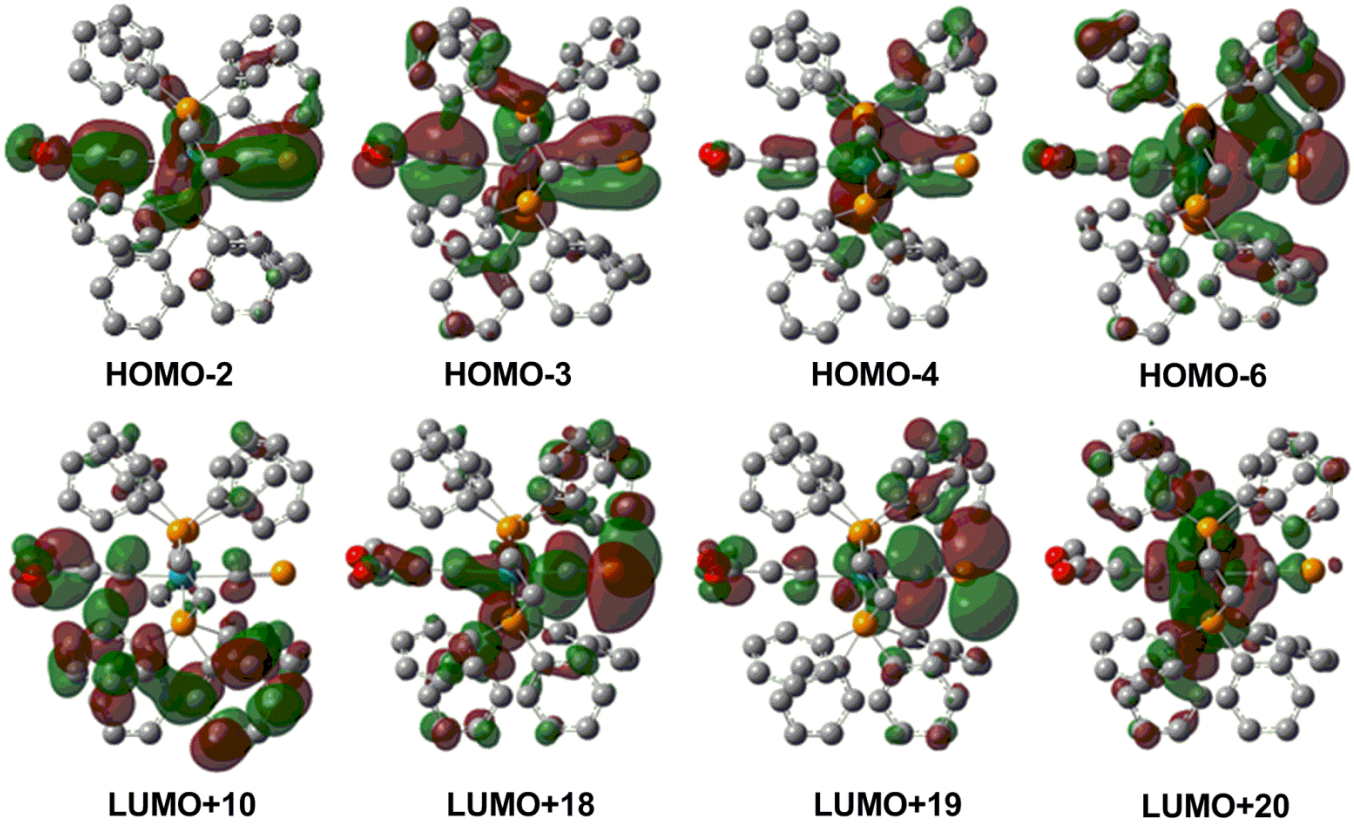

Figure S4. Selected molecular orbitals for **7**

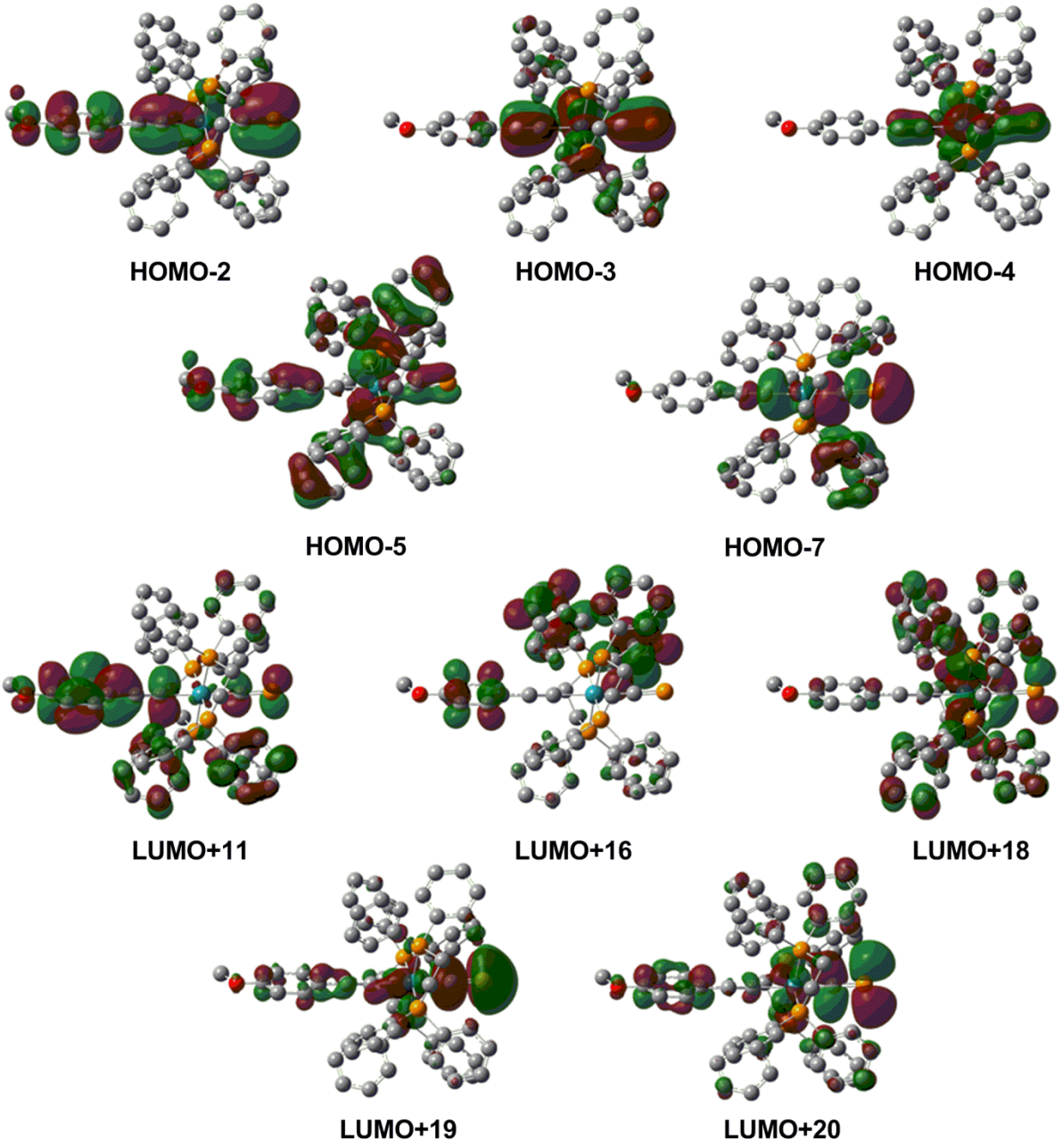

Figure S5. Selected molecular orbitals for **8**.

Table S3. Composition of selected molecular orbitals for **7**.

Orbital	Energy / eV	% Ru	%C≡P	%C≡C	%C=O	%OMe	%dppe1	%dppe2
L+20	0.99	32	3	9	0	0	32	24
L+19	0.82	7	70	2	5	1	4	12
L+18	0.46	7	49	4	1	0	20	18
L+17	0.4	13	21	1	1	0	28	35
L+16	0.25	1	0	0	0	0	8	90
L+15	0.2	2	2	0	0	0	48	48
L+14	0.14	0	2	0	0	0	44	54
L+13	0.05	0	1	0	0	0	87	12
L+12	-0.09	1	4	13	16	2	10	53
L+11	-0.11	1	3	4	6	1	23	63
L+10	-0.18	1	2	7	10	1	11	67
L+9	-0.21	1	0	0	0	0	70	28
L+8	-0.22	1	1	0	0	0	74	23
L+7	-0.33	2	1	1	2	0	64	31
L+6	-0.37	4	2	5	7	1	36	43
L+5	-0.42	1	3	0	0	0	18	78
L+4	-0.45	1	1	1	0	0	23	74
L+3	-0.57	4	2	1	0	0	38	56
L+2	-0.65	2	1	1	0	0	86	9
L+1	-0.74	1	0	1	0	0	93	4
LUMO	**-1.05**	**26**	**0**	**0**	**0**	**0**	**40**	**34**
HOMO	**-4.75**	**35**	**50**	**8**	**2**	**0**	**2**	**2**
H-1	-4.79	34	49	10	2	0	3	2
H-2	-5.76	6	26	34	9	1	11	13
H-3	-5.86	14	19	28	6	0	15	17
H-4	-6.08	74	4	2	0	0	8	11
H-5	-6.3	17	7	2	0	0	29	45
H-6	-6.32	9	24	7	3	0	39	18
H-7	-6.44	8	30	9	1	0	6	47
H-8	-6.56	4	6	2	1	0	29	60
H-9	-6.6	3	1	2	1	0	42	50
H-10	-6.62	3	1	2	3	0	20	70
H-11	-6.66	3	1	1	2	0	18	74
H-12	-6.67	3	0	3	1	0	34	59
H-13	-6.76	2	2	3	1	0	43	50
H-14	-6.8	3	1	1	4	0	50	41
H-15	-6.83	6	2	3	15	1	31	41
H-16	-6.85	1	0	1	4	0	43	51
H-17	-6.89	3	1	2	9	1	45	40
H-18	-6.94	3	3	1	0	0	78	16
H-19	-6.96	5	2	1	0	1	75	16
H-20	-7.01	8	10	3	16	2	25	35

Table S4. Composition of selected molecular orbitals for **8**.

Orbital	Energy / eV	% Ru	%C≡P	%C≡C	%C=O	%OMe	%dppe1	%dppe2
L+20	0.78	9	62	1	7	0	13	8
L+19	0.61	7	68	3	4	0	14	4
L+18	0.43	16	9	1	1	0	30	42
L+17	0.31	1	2	1	7	0	17	72
L+16	0.29	0	1	0	79	1	2	17
L+15	0.25	1	1	0	7	0	13	78
L+14	0.21	1	1	1	4	0	82	10
L+13	0.18	1	3	3	10	1	68	15
L+12	0.14	1	7	8	36	2	25	21
L+11	0.05	1	2	3	12	1	38	44
L+10	-0.06	1	1	0	0	0	29	69
L+9	-0.11	1	0	0	1	0	65	32
L+8	-0.17	1	3	0	0	0	50	45
L+7	-0.19	2	0	0	1	0	48	50
L+6	-0.24	2	0	1	0	0	29	68
L+5	-0.33	0	1	0	1	0	23	75
L+4	-0.4	2	1	1	1	0	62	33
L+3	-0.41	0	1	0	0	0	85	13
L+2	-0.5	3	1	1	0	0	17	78
L+1	-0.52	2	0	0	0	0	89	8
LUMO	**-0.91**	**24**	**0**	**0**	**0**	**0**	**37**	**39**
HOMO	**-4.36**	**30**	**24**	**22**	**17**	**3**	**2**	**2**
H-1	-4.59	35	43	14	2	0	3	3
H-2	-5.08	5	42	16	21	5	5	6
H-3	-5.55	3	26	44	3	0	12	12
H-4	-5.92	80	1	0	0	0	9	9
H-5	-6.12	14	3	2	13	5	30	32
H-6	-6.22	17	12	2	3	1	20	45
H-7	-6.28	9	53	17	1	0	14	7
H-8	-6.38	10	9	5	13	4	24	35
H-9	-6.46	2	1	1	5	0	28	62
H-10	-6.5	2	1	1	58	0	16	23
H-11	-6.54	3	2	2	28	0	52	12
H-12	-6.57	2	0	3	4	1	37	52
H-13	-6.6	6	1	4	0	0	46	43
H-14	-6.62	2	2	0	0	0	33	62
H-15	-6.65	1	2	0	1	0	29	67
H-16	-6.67	2	2	1	1	1	56	38
H-17	-6.71	5	2	4	2	1	35	50
H-18	-6.73	2	1	0	0	0	63	34
H-19	-6.77	1	0	1	1	0	41	56
H-20	-6.81	4	2	5	0	0	49	40

Table S5. First 100 excited states for **7** derived from TD-DFT.

No.	E /cm^{-1}	λ / nm	Osc. Strength	Major contributions
1	21585.16	463.2813	0.0008	HOMO->LUMO (91%)
2	22161.85	451.2259	0.001	H-1->LUMO (91%)
3	27438.36	364.4532	0.0057	HOMO->L+1 (47%), HOMO->L+2 (20%), HOMO->L+3 (24%)
4	27738.4	360.511	0.0019	H-4->LUMO (74%)
5	28139.27	355.3753	0.0033	H-1->L+1 (60%), H-1->L+2 (11%), H-1->L+3 (20%)
6	28234.44	354.1774	0.0021	HOMO->L+1 (25%), HOMO->L+2 (69%)
7	28722.41	348.1602	0.0023	H-1->L+1 (19%), H-1->L+2 (58%), HOMO->L+3 (12%)
8	28810.32	347.0978	0.0005	H-1->L+2 (15%), HOMO->L+1 (20%), HOMO->L+3 (54%)
9	29276.51	341.5707	0.002	H-1->L+1 (14%), H-1->L+2 (11%), H-1->L+3 (68%)
10	29947.57	333.9169	0	HOMO->L+5 (78%)
11	30316.17	329.857	0.001	H-1->L+6 (21%), H-1->L+12 (10%), HOMO->L+4 (37%)
12	30433.93	328.5806	0.0011	H-1->L+5 (49%), HOMO->L+4 (26%)
13	30612.18	326.6674	0.0011	H-1->L+4 (10%), H-1->L+5 (22%), H-1->L+6 (17%), HOMO->L+4 (32%)
14	30855.76	324.0886	0.0021	H-1->L+4 (31%), H-1->L+6 (13%), HOMO->L+6 (22%), HOMO->L+7 (13%)
15	30952.55	323.0752	0.0053	H-1->L+4 (41%), HOMO->L+6 (29%), HOMO->L+7 (10%)
16	31510.69	317.3527	0.011	HOMO->L+6 (24%), HOMO->L+7 (47%), HOMO->L+8 (13%)
17	31544.56	317.0119	0.0012	H-1->L+7 (63%)
18	31968.81	312.8049	0.0049	HOMO->L+7 (18%), HOMO->L+8 (31%), HOMO->L+18 (12%)
19	32272.08	309.8654	0.0376	H-2->LUMO (62%)
20	32422.1	308.4316	0.0148	H-2->LUMO (12%), H-1->L+6 (21%), H-1->L+10 (14%), H-1->L+12 (16%)
21	32567.28	307.0567	0.0267	H-3->LUMO (35%), HOMO->L+10 (11%), HOMO->L+11 (15%)
22	32666.49	306.1241	0.0162	H-1->L+8 (13%), HOMO->L+10 (32%), HOMO->L+12 (10%)
23	32793.12	304.942	0.0013	HOMO->L+9 (80%)
24	32848.77	304.4254	0.0092	H-1->L+8 (33%), HOMO->L+8 (13%), HOMO->L+10 (16%)
25	33060.09	302.4795	0.0096	H-3->LUMO (10%), H-1->L+8 (13%), HOMO->L+8 (17%), HOMO->L+10 (16%), HOMO->L+11 (12%)
26	33244.79	300.799	0.0011	H-1->L+9 (52%), HOMO->L+11 (17%)
27	33351.26	299.8388	0.0035	H-1->L+8 (14%), H-1->L+9 (26%), HOMO->L+11 (22%)
28	33507.73	298.4386	0.0116	H-1->L+10 (23%), H-1->L+12 (12%), HOMO->L+12 (34%)
29	33655.33	297.1298	0.006	H-1->L+10 (12%), H-1->L+11 (71%)
30	33687.59	296.8452	0.011	H-1->L+10 (25%), H-1->L+12 (24%), HOMO->L+12 (15%), HOMO->L+18 (12%)
31	34795	287.3976	0.0023	HOMO->L+13 (86%)
32	34989.38	285.801	0.0017	H-1->L+15 (11%), H-1->L+17 (17%), HOMO->L+15 (14%)
33	35220.06	283.9291	0.0118	H-1->L+13 (58%)
34	35442.67	282.1458	0.0169	H-1->L+13 (21%), H-1->L+15 (11%), HOMO->L+15 (21%), HOMO->L+17 (12%)

35	35550.75	281.2881	0.0132	H-5->LUMO (76%)
36	35607.2	280.842	0.0004	HOMO->L+14 (66%)
37	35772.55	279.544	0.0184	H-1->L+14 (27%)
38	36050.01	277.3925	0.006	HOMO->L+14 (20%), HOMO->L+16 (19%)
39	36202.45	276.2244	0.0056	H-1->L+14 (47%)
40	36336.33	275.2066	0.0114	H-2->L+1 (22%), H-1->L+15 (24%)
41	36410.54	274.6458	0.0151	H-2->L+1 (37%), HOMO->L+15 (12%), HOMO->L+17 (13%)
42	36542.81	273.6516	0.005	HOMO->L+15 (13%), HOMO->L+16 (41%)
43	36653.31	272.8266	0.0119	H-1->L+15 (14%), H-1->L+16 (39%), H-1->L+17 (11%)
44	36717.03	272.3532	0.0103	H-2->L+1 (11%), HOMO->L+16 (21%), HOMO->L+20 (23%)
45	37034.82	270.0162	0.0012	H-1->L+15 (19%), H-1->L+16 (36%), H-1->L+17 (13%)
46	37121.12	269.3884	0.0135	H-6->LUMO (10%), H-3->L+1 (22%), HOMO->L+17 (11%), HOMO->L+20 (12%)
47	37275.98	268.2693	0.0264	H-6->LUMO (11%), H-3->L+1 (44%), H-1->L+20 (10%)
48	37390.51	267.4476	0.1014	H-6->LUMO (46%), H-2->L+3 (10%), H-1->L+20 (14%)
49	37598.6	265.9673	0.005	H-2->L+2 (61%), H-1->L+20 (12%)
50	37940.58	263.57	0.003	H-2->L+3 (65%), H-1->L+20 (13%)
51	38035.76	262.9105	0.0063	H-3->L+2 (78%)
52	38293.05	261.144	0.0174	H-4->L+1 (43%), H-3->L+3 (15%)
53	38505.98	259.6999	0.0382	H-7->LUMO (28%), H-3->L+3 (27%)
54	38539.05	259.4771	0.0819	H-7->LUMO (11%), H-4->L+1 (19%), H-3->L+3 (35%)
55	38623.74	258.9081	0.0705	H-7->LUMO (24%), H-2->L+4 (19%), H-1->L+19 (12%)
56	38952.01	256.7262	0.0464	H-4->L+1 (12%), H-4->L+2 (61%)
57	38981.04	256.5349	0.0275	H-2->L+4 (61%)
58	39207.69	255.052	0.004	H-2->L+5 (87%)
59	39520.63	253.0324	0.0155	H-4->L+2 (15%), H-4->L+3 (60%)
60	39616.61	252.4194	0.0151	H-3->L+5 (83%)
61	39752.92	251.5538	0.0032	H-3->L+4 (79%)
62	40053.77	249.6644	0.0084	H-3->L+6 (20%), H-2->L+6 (42%), H-2->L+7 (11%)
63	40153.78	249.0425	0.0468	H-9->LUMO (13%), H-8->LUMO (50%)
64	40282.83	248.2447	0.0058	H-3->L+6 (31%), H-2->L+7 (42%)
65	40432.05	247.3286	0.015	H-5->L+1 (70%)
66	40534.48	246.7036	0.0009	H-3->L+6 (21%), H-2->L+6 (18%), H-2->L+7 (12%), H-2->L+12 (11%)
67	40686.92	245.7792	0.0094	H-9->LUMO (18%), H-4->L+5 (17%)
68	40790.16	245.1572	0.0037	H-4->L+4 (13%), H-3->L+7 (44%)
69	40919.21	244.384	0.0038	H-4->L+4 (21%), H-3->L+7 (28%)
70	40932.11	244.307	0.0033	H-9->LUMO (16%), H-5->L+2 (30%), H-4->L+5 (30%)
71	41048.26	243.6157	0.0144	H-5->L+2 (33%), H-4->L+4 (21%)
72	41062.78	243.5296	0.0012	H-11->LUMO (14%), H-4->L+5 (29%)
73	41103.91	243.2859	0.0046	H-2->L+8 (62%)
74	41246.67	242.4438	0.015	H-6->L+1 (49%)
75	41364.43	241.7536	0.0055	H-11->LUMO (17%), H-10->LUMO (11%), H-2->L+9 (16%)
76	41379.75	241.6641	0.0003	H-4->L+4 (10%), H-4->L+6 (59%)
77	41479.77	241.0814	0.0029	H-2->L+9 (39%)

78	41561.23	240.6089	0.0015	H-13->LUMO (12%), H-5->L+3 (15%)
79	41576.55	240.5202	0.0232	H-2->L+9 (11%), H-2->L+10 (25%)
80	41638.66	240.1614	0.0248	H-6->L+2 (27%), H-5->L+3 (10%)
81	41671.73	239.9708	0.0053	H-3->L+8 (49%), H-2->L+10 (10%)
82	41774.16	239.3824	0.0018	H-13->LUMO (13%), H-6->L+2 (14%), H-5->L+3 (12%), H-3->L+9 (23%)
83	41838.69	239.0132	0.0179	H-14->LUMO (13%), H-12->LUMO (20%)
84	41908.05	238.6176	0.0092	H-12->LUMO (16%), H-4->L+7 (12%)
85	41967.74	238.2783	0.0215	H-12->LUMO (13%), H-4->L+7 (13%)
86	42047.59	237.8258	0.0076	H-4->L+7 (12%), H-3->L+10 (11%), H-3->L+12 (10%)
87	42086.3	237.607	0.0069	H-7->L+1 (28%)
88	42127.44	237.375	0.0195	H-14->LUMO (35%), H-3->L+9 (12%)
89	42210.51	236.9078	0.0077	H-13->LUMO (12%), H-2->L+11 (31%)
90	42263.74	236.6094	0.0062	H-4->L+7 (19%), HOMO->L+21 (23%)
91	42292.78	236.447	0.0079	H-7->L+1 (17%), H-2->L+11 (14%), HOMO->L+21 (14%)
92	42386.34	235.9251	0.0156	H-6->L+3 (48%), HOMO->L+21 (10%)
93	42493.61	235.3295	0.0178	H-3->L+11 (18%)
94	42504.91	235.267	0.0233	H-1->L+21 (50%)
95	42597.66	234.7547	0.0247	H-15->LUMO (13%), H-7->L+1 (15%), H-3->L+12 (11%)
96	42681.54	234.2933	0.0062	H-5->L+5 (11%), H-3->L+10 (37%), H-3->L+12 (22%)
97	42776.72	233.772	0.0005	H-5->L+5 (58%)
98	42866.24	233.2838	0.0244	H-16->LUMO (24%)
99	42939.64	232.885	0.0225	H-16->LUMO (11%)
100	43000.94	232.5531	0.0047	H-17->LUMO (11%)

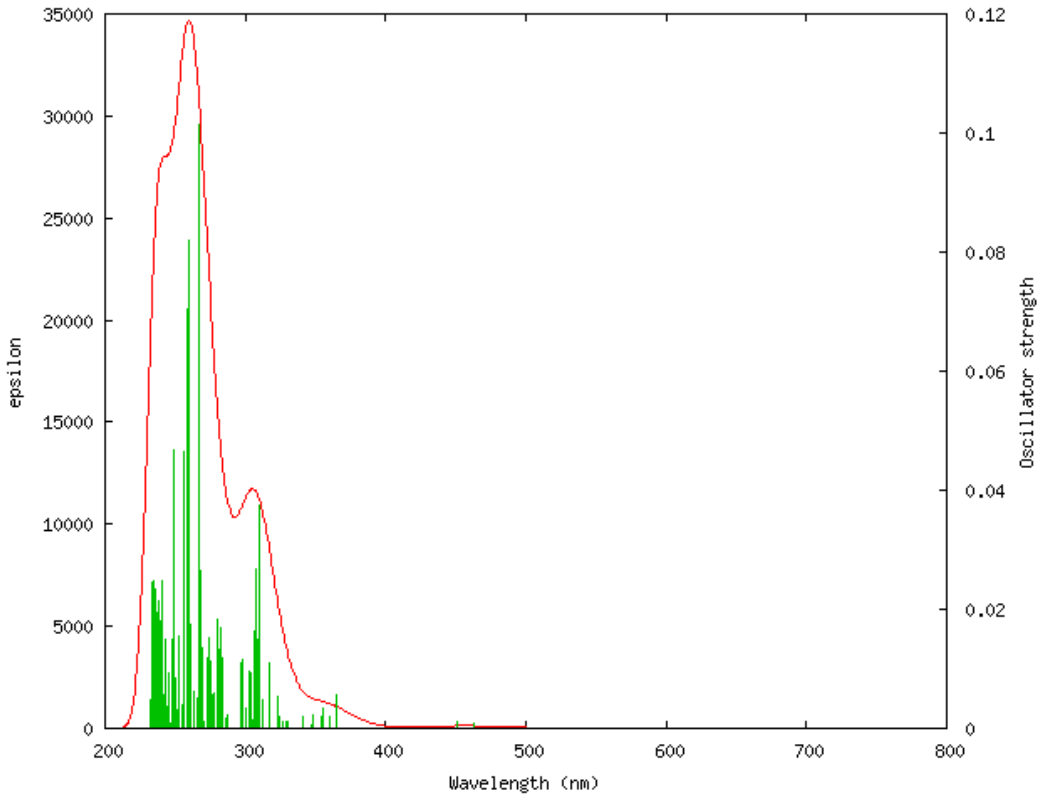

Figure S6: Simulated UV/Vis spectrum for **7**, showing calculated electronic transitions, derived from TD-DFT.

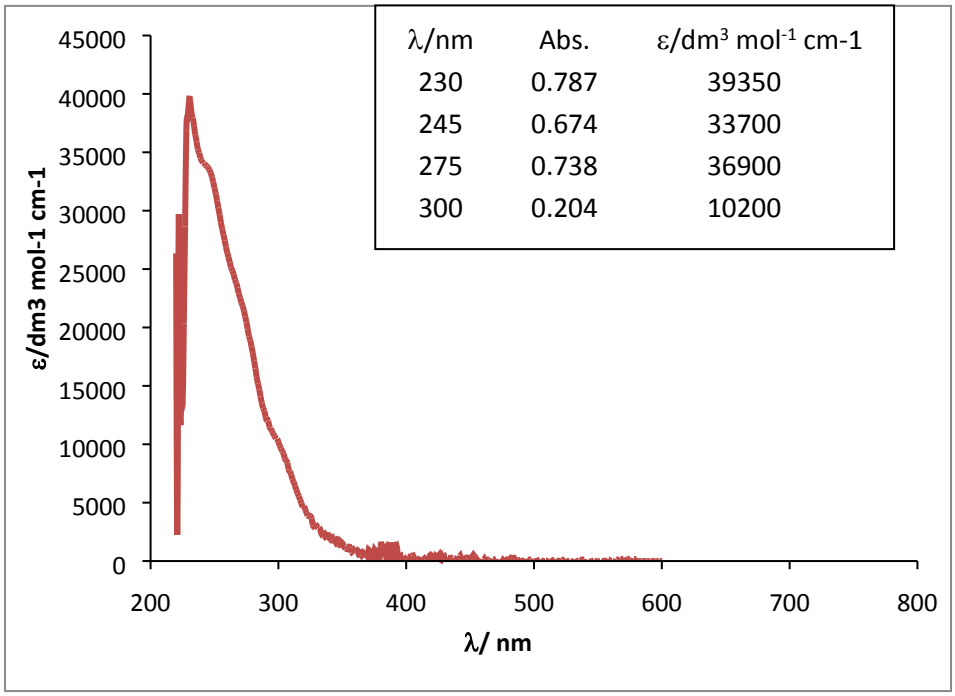

Figure S7: Experimental UV/Vis spectrum for **7**, 2.0 x 10^{-5} mol dm^{-3} in CH_2Cl_2, 1 cm path.

Table S6. First 100 excited states for **8** derived from TD-DFT.

No.	E /cm^{-1}	λ / nm	Osc. Strength	Major contributions
1	22177.98	450.8977	0.001	HOMO->LUMO (87%)
2	23772.55	420.6532	0.0015	H-1->LUMO (88%)
3	27859.39	358.9454	0.0009	HOMO->L+1 (49%), HOMO->L+2 (31%)
4	27934.40	357.9816	0.001	H-4->LUMO (66%), H-3->LUMO (14%)
5	28380.43	352.3555	0.0035	HOMO->L+1 (38%), HOMO->L+2 (56%)
6	29245.06	341.9381	0.0033	HOMO->L+4 (73%)
7	29525.74	338.6875	0.0003	HOMO->L+3 (96%)
8	29747.55	336.1622	0.0085	H-1->L+1 (21%), H-1->L+2 (29%), HOMO->L+5 (23%)
9	29881.43	334.6560	0.0083	H-1->L+1 (23%), HOMO->L+5 (60%)
10	30278.26	330.2699	0.0051	H-1->L+1 (30%), H-1->L+2 (43%)
11	30670.25	326.0489	0.025	HOMO->L+6 (74%)
12	30930.77	323.3027	0.0136	H-2->LUMO (24%), HOMO->L+6 (14%), HOMO->L+7 (12%), HOMO->L+8 (38%)
13	31066.27	321.8925	0.0018	H-1->L+4 (11%), HOMO->L+7 (32%), HOMO->L+8 (24%)
14	31147.73	321.0506	0.0054	H-1->L+3 (19%), H-1->L+5 (17%), HOMO->L+7 (32%)
15	31195.32	320.5609	0.0026	H-1->L+1 (13%), H-1->L+4 (63%)
16	31285.66	319.6353	0.0145	H-2->LUMO (37%), H-1->L+3 (11%), HOMO->L+7 (16%), HOMO->L+8 (17%)
17	31663.13	315.8248	0.0189	H-1->L+3 (49%), H-1->L+5 (23%)
18	31825.24	314.2160	0.0095	H-1->L+5 (12%), HOMO->L+9 (50%), HOMO->L+10 (13%)
19	31903.48	313.4454	0.0668	H-1->L+5 (17%), HOMO->L+9 (45%), HOMO->L+10 (18%)
20	32215.62	310.4084	0.0088	HOMO->L+10 (47%)
21	32493.08	307.7579	0.0866	H-1->L+6 (39%), HOMO->L+11 (28%)
22	32774.57	305.1146	0.0107	H-1->L+6 (39%), H-1->L+8 (40%)
23	33024.60	302.8046	0.0021	H-1->L+7 (82%)
24	33176.23	301.4206	0.0033	HOMO->L+12 (69%)
25	33269.79	300.5730	0.0129	HOMO->L+13 (10%), HOMO->L+18 (18%), HOMO->L+19 (27%)
26	33388.36	299.5056	0.1955	HOMO->L+11 (24%), HOMO->L+19 (12%)
27	33540.80	298.1444	0.0179	H-1->L+8 (12%), H-1->L+9 (31%), H-1->L+11 (18%)
28	33926.33	294.7563	0.0273	H-1->L+9 (14%), H-1->L+10 (56%), HOMO->L+14 (15%)
29	34006.18	294.0642	0.0104	H-1->L+9 (46%), H-1->L+11 (18%)
30	34046.51	293.7159	0.0313	H-1->L+10 (18%), HOMO->L+13 (45%), HOMO->L+14 (25%)
31	34272.35	291.7804	0.0067	HOMO->L+13 (13%), HOMO->L+14 (21%), HOMO->L+15 (38%)
32	34459.47	290.1960	0.0059	HOMO->L+14 (15%), HOMO->L+15 (28%), HOMO->L+18 (13%)
33	34507.06	289.7958	0.0019	HOMO->L+16 (76%)
34	34665.14	288.4742	0.0334	H-1->L+11 (11%), H-1->L+18 (22%), HOMO->L+17 (27%)
35	34889.37	286.6202	0.0594	H-4->LUMO (10%), H-3->LUMO (44%), HOMO->L+17 (19%)
36	34990.19	285.7944	0.0394	H-3->LUMO (23%), HOMO->L+17 (27%), HOMO->L+18 (11%)

37	35190.21	284.1699	0.008	H-1->L+12 (66%)
38	35262.00	283.5914	0.1351	H-1->L+19 (23%), HOMO->L+20 (24%)
39	35385.40	282.6024	0.0255	H-2->L+1 (24%), H-2->L+2 (52%)
40	35520.10	281.5308	0.0041	H-2->L+1 (65%), H-2->L+2 (26%)
41	36053.23	277.3676	0.0306	H-1->L+13 (74%)
42	36219.38	276.0953	0.0156	H-1->L+14 (58%), H-1->L+20 (11%)
43	36307.30	275.4267	0.0033	H-2->L+4 (62%), H-1->L+14 (10%)
44	36406.50	274.6762	0.0027	H-1->L+15 (16%), H-1->L+16 (72%)
45	36513.00	273.8753	0.0058	H-2->L+3 (87%)
46	36646.05	272.8807	0.0061	H-1->L+14 (11%), H-1->L+15 (46%), H-1->L+16 (19%), H-1->L+17 (12%)
47	36686.38	272.5807	0.0133	H-2->L+4 (11%), H-2->L+5 (20%), H-1->L+15 (24%)
48	36834.79	271.4825	0.0001	H-2->L+5 (39%), H-1->L+17 (46%)
49	36924.32	270.8242	0.0232	H-2->L+5 (31%), H-1->L+17 (26%), H-1->L+20 (14%)
50	37174.35	269.0027	0.0108	H-1->L+18 (10%), H-1->L+20 (17%), HOMO->L+21 (33%)
51	37711.52	265.1710	0.0143	H-2->L+6 (83%)
52	38071.25	262.6654	0.0208	H-2->L+7 (83%), H-2->L+8 (11%)
53	38104.31	262.4375	0.0062	H-2->L+7 (12%), H-2->L+8 (62%)
54	38200.29	261.7781	0.0209	H-1->L+21 (50%)
55	38372.90	260.6006	0.0227	H-4->L+1 (11%), H-3->L+1 (18%), H-2->L+8 (16%)
56	38595.51	259.0975	0.1142	H-5->LUMO (61%), H-3->L+1 (11%)
57	38770.53	257.9278	0.0367	H-4->L+2 (27%), H-3->L+1 (21%), H-3->L+2 (29%)
58	38830.22	257.5314	0.0058	H-2->L+9 (84%)
59	39006.85	256.3652	0.0462	H-7->LUMO (26%), H-2->L+10 (43%)
60	39027.02	256.2327	0.0204	H-7->LUMO (19%), H-2->L+10 (48%)
61	39114.93	255.6568	0.0193	H-7->LUMO (15%), H-4->L+1 (10%), H-3->L+1 (20%), H-3->L+2 (32%)
62	39270.60	254.6434	0.013	H-4->L+1 (38%), H-4->L+2 (18%), H-3->L+1 (12%), H-3->L+2 (17%)
63	39396.42	253.8301	0.0376	H-4->L+2 (19%), H-2->L+11 (20%), HOMO->L+20 (12%)
64	39498.86	253.1719	0.0695	H-7->LUMO (14%), H-6->LUMO (41%), H-3->L+4 (10%)
65	39722.27	251.7479	0.0586	H-6->LUMO (15%), H-4->L+4 (19%), H-3->L+4 (38%)
66	39849.71	250.9429	0.0069	H-4->L+3 (27%), H-3->L+3 (56%)
67	40052.96	249.6694	0.006	H-2->L+11 (26%), H-2->L+12 (49%)
68	40138.46	249.1376	0.0214	H-4->L+4 (10%), H-4->L+5 (16%), H-3->L+3 (11%), H-3->L+5 (52%)
69	40259.44	248.3889	0.0099	H-4->L+3 (14%), H-4->L+4 (25%), H-3->L+3 (17%), H-3->L+4 (25%)
70	40349.78	247.8328	0.0053	H-4->L+3 (42%), H-4->L+4 (14%)
71	40403.01	247.5063	0.0072	H-4->L+5 (11%), H-2->L+12 (25%), H-2->L+13 (15%)
72	40636.11	246.0866	0.008	H-4->L+5 (47%), H-3->L+5 (18%)
73	40740.96	245.4532	0.0359	H-2->L+11 (12%), H-2->L+19 (26%)
74	40922.43	244.3647	0.0111	H-8->LUMO (13%), H-4->L+6 (10%), H-3->L+6 (26%), H-3->L+8 (13%)
75	41011.16	243.8361	0.07	H-8->LUMO (22%), H-3->L+6 (20%), H-2->L+13 (12%)
76	41086.17	243.3909	0.0319	H-2->L+14 (71%)
77	41171.66	242.8855	0.0221	H-4->L+6 (11%), H-2->L+13 (42%), H-2->L+15 (17%)

78	41291.03	242.1833	0.0011	H-4->L+6 (15%), H-3->L+7 (12%), H-3->L+8 (10%), H-2->L+15 (25%)
79	41326.52	241.9754	0.0945	H-8->LUMO (21%), H-4->L+8 (19%), H-3->L+8 (24%)
80	41337.81	241.9093	0.0026	H-4->L+7 (10%), H-3->L+7 (45%), H-2->L+15 (16%)
81	41378.95	241.6688	0.0067	H-2->L+16 (76%)
82	41436.21	241.3348	0.0102	H-4->L+6 (24%), H-4->L+8 (14%)
83	41680.60	239.9198	0.0011	H-4->L+6 (19%), H-4->L+8 (26%), H-3->L+6 (19%)
84	41713.67	239.7296	0.0148	H-2->L+17 (58%)
85	41870.14	238.8337	0.0359	H-4->L+7 (28%), H-2->L+18 (32%)
86	41944.35	238.4112	0.0268	H-4->L+7 (27%), H-2->L+17 (11%), H-2->L+18 (22%)
87	42076.62	237.6617	0.0111	H-3->L+8 (10%), H-3->L+9 (34%), H-3->L+11 (15%)
88	42212.93	236.8942	0.0213	H-9->LUMO (22%), H-3->L+10 (10%)
89	42262.93	236.6139	0.0025	H-3->L+9 (20%), H-3->L+10 (13%)
90	42338.75	236.1902	0.033	H-5->L+1 (29%), H-3->L+10 (19%)
91	42391.99	235.8936	0.0158	H-10->LUMO (15%), H-9->LUMO (10%), H-4->L+7 (12%)
92	42491.19	235.3429	0.0267	H-5->L+1 (16%), H-4->L+10 (23%), H-4->L+11 (10%)
93	42588.79	234.8036	0.0024	H-4->L+9 (53%), H-4->L+10 (11%)
94	42608.15	234.6969	0.0024	H-5->L+1 (12%), H-4->L+11 (23%), H-3->L+10 (11%)
95	42725.10	234.0545	0.0197	H-5->L+2 (50%)
96	42764.62	233.8381	0.0093	H-4->L+18 (10%)
97	42848.50	233.3804	0.0075	H-11->LUMO (15%), H-4->L+9 (16%)
98	43014.65	232.4789	0.0087	H-11->LUMO (10%), H-10->LUMO (17%), H-9->LUMO (14%)
99	43177.58	231.6017	0.0029	H-14->LUMO (13%), H-4->L+10 (10%)
100	43230.81	231.3165	0.0405	

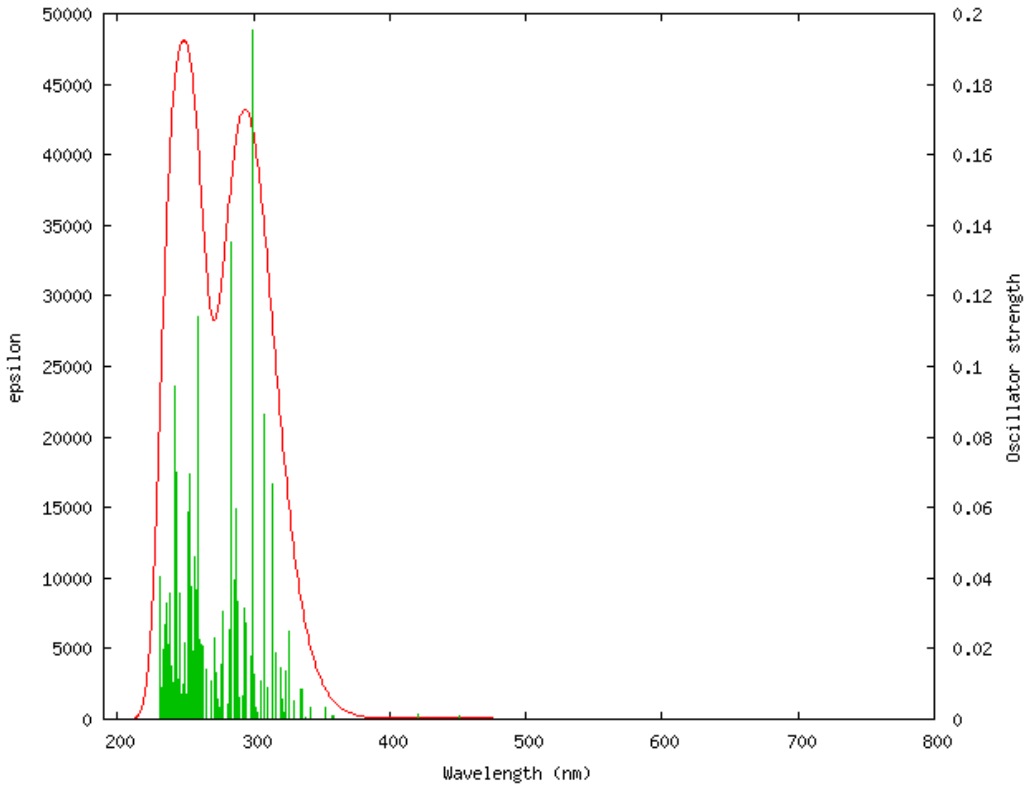

Figure S8: Simulated UV/Vis spectrum for **8**, showing calculated electronic transitions, derived from TD-DFT.

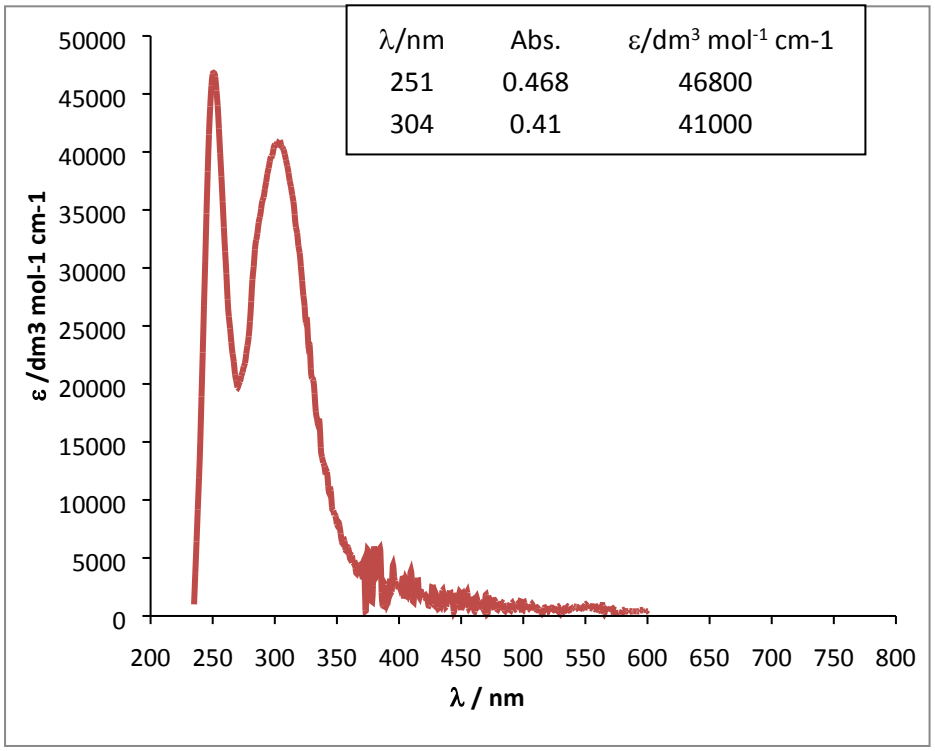

Figure S9: Experimental UV/Vis spectrum for **8**, 1.0 x 10^{-5} mol dm^{-3} in CH_2Cl_2, 1 cm path.

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