Supporting Information

Giant Multi-Photon Absorption by Heptazine Organometalation

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**Supporting Information**

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General Conditions and Reagents

Reactions were performed under a nitrogen atmosphere using standard Schlenk techniques, with no precautions to exclude air during workup. The following solvents, starting materials and catalysts were commercially available, purchased from common chemical suppliers and used as received (unless otherwise specifically mentioned): trimethylsilylacetylene (TMSA), tetra-n-butylammonium fluoride (TBAF, as a 1.0 M solution in THF), anhydrous aluminum trichloride, 1-decanethiol, pyridine, Tf$_2$O (98%), NaH (60% in mineral oil), N,N-diethyl-4-iodoaniline, CuI, ethynylbenzene, NaPF$_6$, NEt$_3$, NH$_4$Cl, NaHCO$_3$, anhydrous MgSO$_4$, n-pentane, methanol, diethyl ether, Celite. The starting material [RuCl(dppe)$_2$]PF$_6$ was synthesized following standard procedures.$^{[1]}$ Reagent grade solvent dichloromethane (Merck) was dried by distilling over calcium hydride and stored under nitrogen, and tetrahydrofuran (THF) (Merck) over sodium/benzophenone. Anisole was dried by refluxing with CaCl$_2$ and stored under nitrogen. N,N-Dimethylformamide (DMF) was dried over activated 4Å molecular sieves. Column chromatography was performed using either alumina or silica (230-400 mesh). Commercially available Pd(PPh$_3$)$_4$ was recrystallized from deoxygenated ethanol and stored under a nitrogen atmosphere before use. The purification followed the standard procedure.$^{[2]}

Melon powder was a gift from Durferrit GmbH, Germany.

The following materials were synthesized based on reported procedures or slight modifications thereof: potassium cyamelurate,$^{[3]}$ cyameluric chloride,$^{[3]}$ 4-nitrophenylacetylene,$^{[4]}$ N,N-diethyl-4-ethynylaniline.$^{[5]}$

Instrumentation

NMR spectra were recorded using Bruker Avance 400 MHz and 600 MHz NMR spectrometers and are referenced to residual CHCl$_3$ (1H, 7.26 ppm), $d_6$-DMSO (1H, 2.50 ppm), CDCl$_3$ (13C, 77.16 ppm), or external 85% H$_3$PO$_4$ (31P, 0.0 ppm). Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer by ATR. UV-Vis spectra were recorded in CH$_2$Cl$_2$ in 1 cm quartz cells using a PerkinElmer Lambda 950 spectrophotometer and are reported as $\lambda_{\text{max}}$ nm (ε 10$^3$ M$^{-1}$ cm$^{-1}$). ESI TOF mass spectra were recorded using a Waters LCT Premier mass spectrometer. Solutions in methanol or acetonitrile were ionized with sodium ions; peaks are reported as m/z (assignment, relative intensity). Microanalyses were carried out at London Metropolitan University. Cyclic voltammetry measurements were recorded using a MacLab 400 interface and MacLab potentiostat from eDAQ Pty Ltd. The supporting electrolyte was 0.1 M (NBu$_4^+$)PF$_6$ in distilled, deoxygenated CH$_2$Cl$_2$; solutions containing ca. 1 $\times$ 10$^{-3}$ M complex were maintained under nitrogen. Measurements were carried out at room temperature using Pt disc working-, Pt wire auxiliary- and Ag/AgCl reference electrodes, such that the
ferrocene/ferrocenium redox couple was located at 0.56 V (peak separation ca. 0.08 V). Scan rates were 100 mV s\(^{-1}\).

The real and imaginary parts of the second hyperpolarizability \(\gamma\) (\(\gamma_{\text{real}}\) and \(\gamma_{\text{imag}}\)) were determined using the Z-scan technique. An amplified femtosecond laser system consisting of an Integra-C regenerative amplifier (Quantronix) operating as an 800 nm pump and a Palitra-FS BIBO crystal-based optical parametric amplifier (Quantronix) were used. The system was tunable over a wavelength range from 650-2520 nm, delivering 130 fs pulses at a 1 kHz repetition rate. The output wavelength was confirmed using an Ocean Optics USB2000+ spectrometer (650-1000 nm) or an Ocean Optics NIRQuest+ spectrometer (950-2500 nm). Coloured glass filters and a Thorlabs polarizing filter were used to remove unwanted wavelengths, and the power was adjusted by use of neutral density filters to obtain nonlinear phase shifts between 0.2 and 1.3 rad. The focal length of the lens used in the experiment was 75 mm, which gave 25-50 \(\mu\)m beam waists resulting in Rayleigh lengths longer than that of the sample thickness. Measurements were made in 1 mm optical cells, such that the total thickness was \(\leq 3\) mm including the glass walls, so results could safely be treated using the thin-sample approximation. Samples travelled down the Z-axis on a Thorlabs motorized stage between -20 and +20 mm (where 0 was the laser focus). Data were collected by three Thorlabs photodiodes, 650-1100 nm with a Si-based detector, 1100-1700 nm with an InGaAs detector, and 1700-2520 nm with an amplified InGaAs detector. Data from the detectors were collected by a Tektronix oscilloscope with a custom LabVIEW program and curve-fitted with theoretical traces computed using equations derived by Sheik-Bahae et al.\(^6\) All measurements were calibrated against closed-aperture Z-scans of the solvent, as well as those of a 3 mm thick silica plate. The real and imaginary components of the second hyperpolarizability (\(\gamma\)) of the materials were calculated assuming additivity of the contributions of the solvent and the solute. Samples were prepared with the concentration around 0.3 w/w\% in deoxygenated and distilled CH\(_2\)Cl\(_2\). Overall, the fitting of data was consistent with 2PA from 800-1550 nm, 3PA from 1600 to 2200 nm and 4PA from 2260 to 2520 nm, although fits at the extrema of these ranges did not necessarily fit the corresponding ideal multiphoton curves, which may suggest that multiple absorptive processes occur at the extrema wavelengths.

Multi-photon absorption cross-sections were calculated using \(^7\):

\[
\sigma_{nPA} = \frac{\alpha_n(h\omega)^{n-1}}{N_0}
\]

where \(n = 2, 3\) and 4, and \(\alpha_n\) is the appropriate nonlinear absorption coefficient, while \(N_0\) is the molecular number density.
NMR Assignments

Proton and carbon labelling of the spectral data for the new compounds started from the heptazine core. For each ruthenium centre, the labelling started from carbons on the diphosphine ethylene group and proceeded through all the carbons on the aromatic rings. All the protons attached to the same carbon atom that are chemically equivalent share the same number. Peaks in the $^{13}$C spectra were assigned with the assistance of 2D spectra H-H COSY, H-C HSQC and H-C HMBC, and were labelled as “C$_{xx}$” (xx represents the atom’s number). Proton peaks were labelled as “H$_{xx}$” in the same manner.

![Chemical structure](image)

**Table S1.** NMR data for s-heptazine derivatives.$^{[a]}$

| Compound                  | $^1$H (ppm) | $^{13}$C (ppm) | $^{31}$P (ppm) |
|---------------------------|-------------|----------------|----------------|
|                           | H$_4$       | H$_5$          | C$_1$          | C$_2$ |  |
| 2,5,8-trianisyl-s-heptazine| 8.56        | 6.99           | 158.0          | 174.7 | -  |
| 1                         | 8.27        | 6.93           | 158.1          | 172.5 | -  |
| 2                         | 8.67        | 7.45           | 159.1          | 174.9 | -  |
| 3                         | 8.50        | 7.60           | 158.8          | 175.4 | -  |
| 4                         | 8.53        | 7.63           | --$^{[b]}$     | --$^{[b]}$ | -  |
| 5                         | 8.52        | 7.58           | 158.4          | 174.9 | -  |
| 6                         | 8.39        | 6.58           | 157.5          | 174.1 | 48.5 |
| 7                         | 8.43        | 6.68           | 157.6          | 174.2 | 53.3 |
| 8                         | 8.47        | 6.80           | 157.7          | 174.4 | 52.8 |
| 9                         | 8.41        | 6.62           | 157.5          | 174.1 | 53.5 |

$^{[a]}$ $^1$H, $^{13}$C and $^{31}$P NMR spectra were measured in CDCl$_3$ solution. $^{[b]}$ A $^{13}$C NMR spectrum of compound 4 could not be obtained due to its low solubility.
Synthesis and Characterization of Organic Compounds

**Synthesis of 2,5,8-tri(1,4-anisyl)-s-heptazine.**[8] This compound was synthesized by a modified procedure and fully characterized. Anhydrous aluminum trichloride (1.31 g, 9.80 mmol, 4.5 eq.) was added to distilled anisole (12 mL) in a dry 50 mL flask. The mixture was heated to 60 °C under nitrogen and then cyameluric chloride (0.60 g, 2.18 mmol, 1.0 eq.) was added to the flask slowly. The reaction was stirred at 60 °C for 2 h under nitrogen until HCl evolution ceased. The solvent was removed under reduced pressure. Water was added to the flask to quench the reaction. The mixture was then stirred vigorously until the color of the solution changed from red to yellow. The crude product was obtained by extraction with water/chloroform, and the organic phase was separated and stirred over anhydrous MgSO₄ and then filtered. The filtrate was reduced in volume to afford a powder that was further purified by trituration in MeOH (30 mL), collected by filtration, and washed with n-pentane, to afford a yellow powder identified as 2,5,8-tri(4-anisyl)-s-heptazine (0.832 g, 1.70 mmol, 78%).

**1H NMR** (400 MHz, CDCl₃) δ 8.57 (d, J = 8.0 Hz, 6H, H₄), 6.99 (d, J = 8.0 Hz, 6H, H₅), 3.92 (s, 9H, HMe) ppm. **13C NMR** (151 MHz, CDCl₃) δ 174.7 (C₂), 165.3 (C₆), 158.0 (C₁), 133.1 (C₄), 126.9 (C₃), 114.1 (C₅), 55.8 (CMe) ppm. IR: v(C=N) 1575 cm⁻¹. UV-Vis (CH₂Cl₂, vmax in cm⁻¹, [ε] in 10⁵ M⁻¹ cm⁻¹): 27050 [120], 31150 [55.1]. HR ESI TOF MS: Calcd. for C₂₇H₂₂N₇O₃: 492.1779; Found: 492.1772 ([M + H]⁺). Anal. Calcd. for C₂₇H₂₁N₇O₃: C, 65.98; H, 4.31; N, 19.95%; Found: C, 65.98; H, 4.29; N, 19.86%.
Synthesis of 2,5,8-tri(1,4-hydroxyphenyl)-s-heptazine (1). Decanethiol (3.25 mL, 13.6 mmol, 15.0 eq.) was added to dry DMF (50 mL) in a 100 mL Schlenk flask, followed by NaH (0.33 g, 60% in mineral oil, 8.15 mmol, 9.0 eq.). The solution was stirred for 10 min at room temperature. 2,5,8-Tri(4-anisyl)-s-heptazine (0.442 g, 0.91 mmol) was added and the reaction was heated at 115 °C for 2 days. After cooling to room temperature, the reaction mixture was filtered, and the product was washed with HCl solution (30 mL, 1 M) and distilled water until the color of the product changed from red to yellow. Further purification by dissolving the product in MeOH, precipitating it from diethyl ether, collecting it, and drying it under vacuum gave a yellow solid identified as 1 (0.364 g, 0.81 mmol, 89%).

$^1$H NMR (400 MHz, $d_6$-DMSO) δ 8.27 (d, $J = 8.5$ Hz, 6H, H$_4$), 6.94 (d, $J = 8.5$ Hz, 6H, H$_5$). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 172.5 (C$_2$), 163.1 (C$_6$), 158.1 (C$_1$), 131.9 (C$_4$), 125.4 (C$_3$), 115.7 (C$_5$) ppm. IR: ν(C=N) 1577 cm$^{-1}$. UV-Vis (EtOH, $\nu_{max}$ in cm$^{-1}$, [ε] in 10$^3$ M$^{-1}$ cm$^{-1}$): 26950 [120.3], 31150 [55.1]. HR ESI MS: Calcd. for C$_{24}$H$_{21}$N$_7$O$_3$: 450.1309; Found: 450.1305 [M + H]$^+$. This compound tenaciously retains water, presumably via H-bonding, and reproducibly analyzes as a trihydrate. Anal. Calcd. for C$_{24}$H$_{21}$N$_7$O$_3$·3H$_2$O: C, 57.25; H, 4.20; N, 19.07%; Found: C, 57.54, H, 3.39, N, 19.21%.

Synthesis of 2,5,8-tri(1,4-triflatophenyl)-s-heptazine (2). CH$_2$Cl$_2$ (50 mL) and distilled pyridine (0.33 mL, 4.04 mmol, 4.2 eq.) were added to a 100 mL flask and the solvent mixture cooled to 0 °C under nitrogen. Tf$_2$O (0.65 mL, 98%, 3.75 mmol, 3.9 eq.) was added dropwise by syringe and then 1 (0.430 g, 0.96 mmol) was added to the stirring solution. The reaction was slowly warmed to room temperature and stirred under nitrogen overnight. The reaction was
quenched by adding saturated NaHCO₃ solution (30 mL). After extraction with CH₂Cl₂/water, the organic phase was collected and dried over anhydrous MgSO₄, and the solvent was removed in vacuo. Further purification by precipitation of a CH₂Cl₂ extract from EtOH afforded 2 as an orange solid (0.679 g, 0.80 mmol, 83%).

¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, J = 9.0 Hz, 6H, H₆), 7.45 (d, J = 9.0 Hz, 6H, H₅). ¹³C NMR (151 MHz, CDCl₃) δ 174.9 (C₂), 159.1 (C₁), 154.0 (C₃), 133.9 (C₀), 132.9 (C₄), 121.9 (C₅), 118.7 (q, J = 321 Hz, C₁(13F₃)) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -72.7 ppm. IR: ν(C≡N) 1588 cm⁻¹. UV-Vis (CH₂Cl₂, v_max in cm⁻¹, [ε] in 10³ M⁻¹ cm⁻¹): 30600 [66.6], 31750 [65.1]. HR ESI MS: Calcd. for C₂₇H₁₃F₀N₇O₉S₃: 845.9788; Found: 845.9792 [M + H]+. Anal. Calcd. for C₂₇H₁₂F₅N₇O₉S₃: C, 38.46; H, 1.41; N, 11.50%; Found: C, 38.46, H, 1.41, N, 11.50%.

**Synthesis of 2,5,8-(1,4-Me₅SiC≡CC₆H₄)₃-s-heptazine (3).** Catalytic amounts of Pd(PPh₃)₄ and CuI, followed by TMSA (2.3 mL, 16.1 mmol, 20.0 eq.), were added to a deoxygenated solution of 2 (0.680 g, 0.80 mmol) in a mixture of NEt₃ (30 mL) and DMF (10 mL). The reaction mixture was sealed and heated at 65 °C for 2 days. After cooling to room temperature, saturated NH₄Cl solution (30 mL) was added to quench the reaction, followed by extraction with water/CH₂Cl₂ three times. The organic phase was collected and dried over anhydrous MgSO₄. The solvent was removed, and the resultant solid was collected and purified by trituration in MeOH (30 mL), to give a yellow solid identified as 3 (0.490 g, 0.72 mmol, 89%).

¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 8.5 Hz, 6H, H₆), 7.60 (d, J = 8.5 Hz, 6H, H₅), 0.28 (s, 27H, H_TMS) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 175.4 (C₁), 158.4 (C₂), 133.7 (C₃), 132.3 (C₄), 129.8 (C₅), 104.4 (C₆), 99.8 (C₇), 0.0 (C_TMS) ppm. IR: ν(C-H) 2923 cm⁻¹, ν(C≡C) 2154 cm⁻¹, ν(C≡N) 1588 cm⁻¹. UV-Vis (CH₂Cl₂, v_max in cm⁻¹, [ε] in 10³ M⁻¹ cm⁻¹): 27100 [61.8], 31550 [18.9]. HR ESI MS: Calcd. for C₃₉H₃₀N₇S₃: 690.2653. Found: 690.2650. Anal. Calcd. for C₃₉H₃₀N₇S₃: C, 67.88; H, 5.70; N, 14.21%; Found: C, 67.84; H, 5.81; N, 14.06%.

**Synthesis of 2,5,8-(1-Et₂NC₆H₄-4-C≡C-1,4-C₆H₄)₃-s-heptazine (5).** Compound 3 (0.490 g, 0.71 mmol) was added to CH₂Cl₂ (50 mL), and TBAF (3.5 mL, 1 M, 5.0 eq.) was then added by syringe. The reaction was stirred at room temperature for 1 h, and then quenched by adding MeOH (30 mL) to the flask. Reduction in volume of the solvent in vacuo afforded a solid that was collected by filtration and washed with n-pentane, to give 2,5,8-(1,4-HC≡CC₆H₄)₃-s-heptazine (4) as a yellow powder (0.241 g, 0.51 mmol, 72%). ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, J = 8.5 Hz, 6H, H₆), 7.64 (d, J = 8.5 Hz, 6H, H₅), 3.33 (s, 3H, H₈) ppm. IR: ν(C≡C) 2102 cm⁻¹, ν(C≡N) 1591 cm⁻¹. HR ESI MS: Calcd. for C₃₀H₁₃N₇: 474.1467. Found: 474.1461 [M + H]+. Compound 4 (0.120 g, 0.25 mmol), N,N-diethyl-4-idoaniline (0.314 g, 1.14 mmol, 4.5 eq.) and deoxygenated solvent (NEt₃/DMF 1:1, 60 mL) were added to a 100 mL flask. Catalytic amounts of Pd(PPh₃)₄ and CuI were added to the flask. The reaction mixture was stirred at 65 °C overnight. After cooling to room temperature, saturated NH₄Cl solution (30 mL) was added to quench the reaction, followed by extraction with water/CHCl₃ three times.
The organic phase was collected, dried over anhydrous MgSO₄, filtered, and the solvent reduced in volume in vacuo, affording a solid that was further purified by trituration in MeOH, to afford 5 as a purple solid (0.187 g, 0.20 mmol, 81%).

1H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 8.3 Hz, 6H, H₄), 7.58 (d, J = 8.3 Hz, 6H, H₅), 7.40 (d, J = 8.7 Hz, 6H, H₁₁), 6.61 (d, J = 8.7 Hz, 6H, H₁₀), 3.38 (q, J = 7.0 Hz, 12H, H₁₂), 1.19 (t, J = 7.0 Hz, 18H, H₈₋₁₉) ppm. 13C NMR (151 MHz, CDCl₃) δ 174.9 (C₂), 157.5 (C₁), 158.4 (C₁), 148.2 (C₁₂), 133.6 (C₁₁), 132.5 (C₈), 131.2 (C₆), 131.1 (C₅), 130.5 (C₄), 111.3 (C₁₀), 108.3 (C₈), 96.7 (C₉), 88.0 (C₇), 44.5 (Cₑ₉₋₁₁), 12.8 (Cₑ₈₋₁₉) ppm. IR: ν(C=N) 1578 cm⁻¹. UV-Vis (CH₂Cl₂, vₘₐₓ in cm⁻¹, [ε] in 10³ M⁻¹ cm⁻¹): 19700 [49.8]. HR ESI MS: Calcd. for C₆₀H₅₅N₁₀: 915.4506. Found: 915.4603 [M + H]⁺. Anal. Calcd. for C₆₀H₅₄N₁₀: C, 78.75; H, 5.95; N, 15.31%; Found: C, 78.47; H, 5.76; N, 15.07%.

Synthesis and Characterization of Metal Complexes

![Synthesis and Characterization of Metal Complexes](image)

**Synthesis of 2,5,8-{trans-[(dppe)₂Cl][Ru(C≡C-1,4-C₆H₄)]₃}s-heptazine (6).** trans-[RuCl(dppe)₂]PF₆ (0.250 g, 0.23 mmol, 3.3 eq.) and compound 4 (0.033 g, 0.070 mmol, prepared as above) were suspended in deoxygenated distilled CH₂Cl₂ (60 mL) and the reaction mixture was refluxed under nitrogen overnight. NET₃ (0.5 mL) was added to the flask and the reaction was stirred under nitrogen for 15 min. The solution was then passed through a Celite pad and the solvent was removed from the filtrate in vacuo. The residue was dissolved in CH₂Cl₂ (5 mL) and added to stirring MeOH (50 mL), affording a precipitate that was collected by filtration and washed with n-pentane, to give a deep blue solid identified as 6 (0.200 g, 0.061 mmol, 84 %).

1H NMR (400 MHz, CDCl₃): δ 8.40 (d, J = 8.5 Hz, 6H, H₄), 7.41-7.38 (m, 48H, H[Ru]-3, H[Ru]-7), 7.23-7.20 (m, 24H, H[Ru]-5, H[Ru]-9), 7.04-6.97 (m, 48H, H[Ru]-4, H[Ru]-8), 6.59 (d, J = 8.5 Hz, 6H, H₅), 2.71 (m, 24H, H[Ru]-1) ppm. 13C NMR (151 MHz, CDCl₃) δ 174.1 (C₂), 157.5 (C₁), 137.2 (C₃), 136.0, 135.7 (m, C[Ru]-2, C[Ru]-6), 134.6, 134.2 (C[Ru]-3, C[Ru]-7), 130.9 (C₈), 130.3, 130.2 (C₄, C₅), 129.2, 129.1 (C[Ru]-5, C[Ru]-9), 128.2 (C₇), 127.5, 127.3 (C[Ru]-4, C[Ru]-8), 118.5 (C₆), 30.7 (C[Ru]-1) ppm. 31P NMR (162 MHz, CDCl₃) δ 48.5 ppm. IR: ν(C≡C) 2050 cm⁻¹, ν(C=N) 1559 cm⁻¹. UV-Vis (CH₂Cl₂, vₘₐₓ in cm⁻¹, [ε] in 10³ M⁻¹ cm⁻¹): 16700 [60.4], 22800 [29.5]. HR ESI MS: Calcd. for [M - 3Cl]³⁺: 1054.8824, [M - 3Cl + 3MeCN]³⁺:1095.9067.
Found: 1054.8837 ([M - 3Cl]^{3+}, 74), 1095.9087 ([M - 3Cl + 3MeCN]^{3+}, 100). Anal. Calcd. for C_{186}H_{156}Cl_{4}N_{7}P_{12}Ru_{3}: C, 68.31; H, 4.81; N, 3.00%; Found: C, 67.95; H, 4.73; N, 3.16%.

**Synthesis of 2,5,8-{trans-[(dppe)_{2}(PhC≡C)Ru(C≡C-1,4-C_{8}H_{4})]_{3}}-s-heptazine (7).** Compound 6 (0.124 g, 0.038 mmol) and ethynylbenzene (0.10 mL, 0.92 mmol, 24.0 eq.) were added to distilled CH_{2}Cl_{2} (50 mL), and NEt_{3} (1 mL) was added to the solution. NaPF_{6} (0.103 g, 0.608 mmol, 16.0 eq.) was added to the flask, and the reaction was heated under reflux for 24 h. The reaction mixture was cooled to room temperature, passed through a Celite pad, and the eluate reduced in volume, affording a solid that was dissolved in CH_{2}Cl_{2}, precipitated by addition to MeOH, collected, dissolved in CH_{2}Cl_{2} again, and precipitated by addition to n-pentane, to afford 7 as a blue powder (0.118 g, 0.034 mmol, 90%).

{\textsuperscript{1}}H NMR (400 MHz, CDC_{13}): δ 8.43 (d, J = 8.5 Hz, 6H, H_{4}), 7.72-7.71 (m, 24H, H_{[Ru]-3} or H_{[Ru]-7}), 7.35-7.33 (m, 24H, H_{[Ru]-3} or H_{[Ru]-7}), 7.22-7.18 (m, 24H, H_{[Ru]-5}, H_{[Ru]-9}), 7.17-7.15 (m, 6H, H_{13}), 7.04-7.04 (m, 3H, H_{14}), 7.01-6.94 (m, 48H, H_{[Ru]-4}, H_{[Ru]-8}), 6.94 (d, J = 8.5 Hz, 6H, H_{12}), 6.88 (d, J = 8.5 Hz, 6H, H_{3}), 2.65 (m, 24H, H_{[Ru]-1}) ppm. {\textsuperscript{13}}C NMR (151 MHz, CDC_{13}) δ 174.2 (C_{2}), 157.6 (C_{1}), 137.4 (C_{3}), 137.2-136.7 (C_{[Ru]-2}, C_{[Ru]-6}), 134.6, 134.1 (C_{[Ru]-3}, C_{[Ru]-7}), 130.6 (C_{4}), 130.2 (C_{5}), 130.1 (C_{12}), 129.0, 128.9 (C_{[Ru]-5}, C_{[Ru]-9}), 128.4 (C_{14}), 127.7 (C_{13}), 127.3 (C_{[Ru]-4}, C_{[Ru]-8}), 123.3 (C_{11}), 120.7 (C_{6}), 31.6 (C_{[Ru]-1}) ppm. {\textsuperscript{31}}P NMR (162 MHz, CDC_{13}) δ 53.3 ppm. IR: υ(C≡C) 2047 cm\(^{-1}\), υ(C=N) 1560 cm\(^{-1}\). UV-Vis (CH_{2}Cl_{2}, v_{max} in cm\(^{-1}\), [ε] in 10\(^3\) M\(^{-1}\) cm\(^{-1}\)): 16650 [102.3], 23100 [60.4]. Anal. Calcd. for C_{213}H_{183}N_{7}P_{12}Ru_{3}: C, 72.77; H, 5.25; N, 2.79%; Found: C, 72.83; H, 4.71; N, 2.83%.

**Synthesis of 2,5,8-{trans-[(dppe)_{2}(4-O_{2}N-C_{8}H_{4}-1-C≡C)Ru(C≡C-1,4-C_{8}H_{4})]_{3}}-s-heptazine (8).** Compound 6 (0.125 g, 0.038 mmol, 1.0 eq.) and 4-nitrophenylacetylene (0.025 g, 0.15 mmol, 4.0 eq.) were added to distilled CH_{2}Cl_{2} (50 mL) and NEt_{3} (1 mL) was added to the solution. NaPF_{6} (0.062 g, 0.35 mmol, 9.0 eq.) was added to the flask and the reaction was stirred at 35 °C overnight, cooled to room temperature, and then passed through a Celite pad. The solvent was removed from the eluate in vacuo, and the residue dissolved in CH_{2}Cl_{2}, precipitated by addition to MeOH, collected, dissolved in CH_{2}Cl_{2} again, and precipitated by addition to n-pentane, affording 8 as a deep-red powder (0.122 g, 0.034 mmol, 89%).

{\textsuperscript{1}}H NMR (400 MHz, CDC_{13}): δ 8.47 (d, J = 8.3 Hz, 6H, H_{4}), 8.01 (d, J = 8.5 Hz, 6H, H_{13}), 7.47 (m, 48H, H_{[Ru]-3}, H_{[Ru]-7}), 7.25-7.20 (m, 24H, H_{[Ru]-5}, H_{[Ru]-9}), 7.02-6.99 (m, 48H, H_{[Ru]-4}, H_{[Ru]-8}), 6.80 (d, J = 8.3 Hz, 6H, H_{5}), 6.65 (d, J = 8.5 Hz, 6H, H_{12}), 2.65 (m, 24H, H_{[Ru]-1}) ppm. {\textsuperscript{13}}C NMR (151 MHz, CDC_{13}) δ 174.4 (C_{2}), 157.7 (C_{1}), 151.6, 148.4 (C_{[Ru]-2}, C_{[Ru]-6}), 143.0 (C_{14}), 137.3, 137.1 (C_{3}), 136.4 (C_{8}, C_{9}), 134.2, 134.1 (C_{[Ru]-3}, C_{[Ru]-7}), 130.4 (C_{4}), 130.2 (C_{5}), 130.0 (C_{12}), 129.23, 129.19 (C_{[Ru]-5}, C_{[Ru]-9}), 128.9 (C_{7}), 127.5, 127.4 (C_{[Ru]-4}, C_{[Ru]-8}), 123.6 (C_{13}), 121.7 (C_{6}), 120.2 (C_{11}), 31.5 (C_{[Ru]-1}) ppm. {\textsuperscript{31}}P NMR (162 MHz, CDC_{13}) δ 52.8 ppm. IR: υ(C≡C) 2040 cm\(^{-1}\), υ(C=N) 1560 cm\(^{-1}\). UV-Vis (CH_{2}Cl_{2}, v_{max} in cm\(^{-1}\), [ε] in 10\(^3\) M\(^{-1}\) cm\(^{-1}\)): 17150 [114], 21600 [75.3]. Anal. Calcd. for C_{210}H_{168}N_{10}O_{3}P_{12}Ru_{3}: C, 70.01; H, 4.70; N, 3.89%; Found: C, 69.87; H, 4.70; N, 3.99%.
Synthesis of 2,5,8-{trans-[(dppe)2(4-Et2NC6H4-1-C≡C)Ru(C≡C-1,4-C6H4)]3-s-heptazine (9). Compound 6 (0.125 g, 0.038 mmol) and N,N-diethyl-4-ethynylaniline (0.033 g, 0.17 mmol, 4.5 eq.) were added to distilled CH2Cl2 (50 mL), and triethylamine (1 mL) was added to the solution. NaPF6 (0.062 g, 0.35 mmol, 9.0 eq.) was added to the flask and the reaction was stirred at 35 °C overnight, cooled to room temperature, and then passed through a Celite pad. The solvent was removed from the eluate and the residue was dissolved in CH2Cl2, precipitated by addition to MeOH, collected, dissolved in CH2Cl2 again, and precipitated by addition to n-pentane, affording 9 as a blue-green solid (0.100 g, 0.027 mmol, 71%).

$^1$H NMR (400 MHz, CDCl3) δ 8.41 (d, $J = 8.3$ Hz, 6H, H4), 7.79-7.28 (m, 48H, H[Ru]-7), 7.22-7.17 (m, 24H, H[Ru]-5, H[Ru]-9), 7.03-6.94 (m, 48H, H[Ru]-4, H[Ru]-8), 6.84 (d, $J = 8.6$ Hz, 6H, H13), 6.62 (d, $J = 8.3$ Hz, 6H, H5), 6.57 (d, $J = 8.6$ Hz, 6H, H12), 3.36 (q, $J = 7.0$ Hz, 12H, HEt-1), 2.63 (m, 24H, H[Ru]-1), 1.20 (t, $J = 7.0$ Hz, 18H, HEt-2) ppm. $^{13}$C NMR (151 MHz, CDCl3) δ 174.1 (C2), 157.5 (C1), 144.6 (C14), 137.5, 136.8 (C[Ru]-2, C[Ru]-6), 134.8, 134.1 (C[Ru]-3, C[Ru]-7), 131.0 (C13), 130.3 (C3), 130.2 (C4), 128.9, 128.8 (C[Ru]-5, C[Ru]-9), 128.2 (C3 or C6), 127.3 (C[Ru]-4, C[Ru]-8), 120.7 (C6 or C3), 119.0 (C10), 118.4 (C11), 111.8 (C12), 44.5 (CEt-1), 31.6 (C[Ru]-1), 13.1 (CEt-2) ppm. $^{31}$P NMR (162 MHz, CDCl3) δ 53.5 ppm. IR: $\nu$(C≡C) 2046 cm$^{-1}$, $\nu$(C=N) 1559 cm$^{-1}$. UV-Vis (CH2Cl2, $\nu$max in cm$^{-1}$, [ε] in 10$^3$ M$^{-1}$ cm$^{-1}$): 16250 [85.6], 22050 [55.5]. Anal. Calcd. for C$_{222}$H$_{198}$N$_{10}$P$_{12}$Ru$_3$: C, 72.44; H, 5.42; N, 3.81%; Found: C, 72.29; H, 5.54; N, 3.86%.
NMR Spectra of New Compounds

Figure S1. $^1$H NMR spectrum of 2,5,8-tri(1,4-anisyl)-s-heptazine in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water.

Figure S2. $^{13}$C NMR spectrum of 2,5,8-tri(1,4-anisyl)-s-heptazine in CDCl$_3$. The peak marked * corresponds to CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of 1 in $d_6$-DMSO. The peaks marked * * are from $d_6$-DMSO. The peak marked # corresponds to residual water.

Figure S4. $^{13}$C NMR spectrum of 1 in $d_6$-DMSO. The peaks marked * * are from $d_6$-DMSO.
Figure S5. $^1$H NMR spectrum of 2 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water.

Figure S6. $^{13}$C NMR spectrum of 2 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$. 
Figure S7. $^{19}$F NMR spectrum of 2 in CDCl$_3$.

Figure S8. $^1$H NMR spectrum of 3 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water.
Figure S9. $^{13}$C NMR spectrum of 3 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$.

Figure S10. $^1$H NMR spectrum of 4 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water. The peak marked * corresponds to residual petrol.
Figure S11. $^1$H NMR spectrum of 5 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water.

Figure S12. $^{13}$C NMR spectrum of 5 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$. 
Figure S13. $^1$H NMR spectrum of 6 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water. The peak marked * corresponds to silicone grease.

Figure S14. $^{13}$C NMR spectrum of 6 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$. 
Figure S15. $^{31}\text{P}$ NMR spectrum of 6 in CDCl$_3$.

Figure S16. $^1\text{H}$ NMR spectrum of 7 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water.
Figure S17. $^{13}$C NMR spectrum of 7 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$.

Figure S18. $^{31}$P NMR spectrum of 7 in CDCl$_3$. 
Figure S19. $^1$H NMR spectrum of 8 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$.
The peak marked # corresponds to residual water.

Figure S20. $^{13}$C NMR spectrum of 8 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$. 
Figure S21. $^3$P NMR spectrum of 8 in CDCl$_3$.

Figure S22. $^1$H NMR spectrum of 9 in CDCl$_3$. The peak marked ** corresponds to residual CHCl$_3$. The peak marked # corresponds to residual water.
Figure S23. $^{13}$C NMR spectrum of 9 in CDCl$_3$. The peak marked ** corresponds to CDCl$_3$.

Figure S24. $^{31}$P NMR spectrum of 9 in CDCl$_3$. 
MS, UV-Vis, Cyclic Voltammetry and Z-scan Studies

**Figure S25.** ESI TOF mass spectra of the [M - 3Cl]^{3+} ion (composition C_{186}H_{156}N_{7}P_{12}Ru_{3}) from 6 showing the experimental (top) and calculated (bottom) isotope distribution.
Figure S26. ESI TOF mass spectra of the $[M - 3\text{Cl} + 3(\text{MeCN})]^{3+}$, $[M - 3\text{Cl} + 2(\text{MeCN})]^{3+}$ and $[M - 3\text{Cl} + \text{MeCN}]^{2+}$ ions from compound 6 [experimental (top) and calculated (bottom) isotope distributions for each ion].
Table S2. Solvatochromic behaviour of compounds 5-9.

| Compound | $\nu_{\text{max}}$ (cm$^{-1}$) |
|----------|---------------------------------|
|          | (toluene)                       |
|          | ($\varepsilon[a] = 2.38$)       |
|          | (THF)                           |
| ($\varepsilon[a] = 7.52$) |
| 5        | 20 500                          |
| 6        | 17 800                          |
| 7        | 17 850                          |
| 8        | 18 400                          |
| 9        | 17 400                          |

[a] $\varepsilon$: dielectric constant.

Figure S27. UV-vis spectra of $s$-heptazine-cored organic compound 5 and ruthenium complexes 6-9.
Table S3. Linear optical data for 5-9 and related compounds.[a]

| Compound | $\nu_{\text{max}}$ (CH$_2$Cl$_2$) | $\nu_{\text{max}}$ (CHCl$_3$) | $\nu_{\text{max}}$ (THF) | $\nu_{\text{max}}$ (toluene) | Ref. |
|----------|-------------------------------|-------------------------------|--------------------------|-------------------------------|-----|
| 6c       | 26 250                        | -                             | -                        | -                             | 9   |
| 7c       | 26 300                        | -                             | -                        | -                             | 9   |
| 6b       | -                             | 21 800                        | -                        | -                             | 10  |
| 8b       | -                             | 21 750                        | -                        | -                             | 10  |
| 10       | -                             | 21 200                        | -                        | -                             | 10  |
| 6a       | -                             | -                             | 24 200                   | -                             | 11,12 |
| 7a       | -                             | -                             | 24 000                   | -                             | 11,12 |
| 8a       | -                             | -                             | 21 800                   | -                             | 11,12 |
| 9a       | -                             | -                             | 24 350                   | -                             | 11,12 |
| 11       | -                             | -                             | -                        | 20 800 [b]                   | 13  |
| 5        | 19 700                        | 19 450                        | 21 000                   | 20 500                        | this work |
| 6        | 16 700                        | 17 800                        | 17 900                   | 17 800                        | this work |
| 7        | 16 650                        | 16 300                        | 18 000                   | 17 850                        | this work |
| 8        | 17 150                        | 16 950                        | 18 650                   | 18 400                        | this work |
| 9        | 16 250                        | 15 850                        | 17 550                   | 17 400                        | this work |

[a] All spectra were recorded at room temperature. Spectral maxima are reported in cm$^{-1}$. [b] Absorption spectrum was recorded with a 100 ms delay in oxygen-free toluene.$^{[12]}$
Table S4. Cyclic voltammetric data for 6c, 6a-9a and 6-9.[a]

| Complex | E_{1/2} [i_{pc}/i_{pa}, ΔE_p] | Ref. |
|---------|--------------------------------|------|
| Ru^{II/III} |                                 |      |
| 6c      | 0.51 [1, 0.06]                 | 9    |
| 6a      | 0.51 [1, 0.06]                 | 11   |
| 7a      | 0.54 [1, 0.06]                 | 11   |
| 8a      | 0.66 [1, 0.06]                 | 11   |
| 9a      | 0.23 [1, 0.06]                 | 11   |
| 6       | 0.67 [1, 0.08]                 | this work |
| 7       | 0.55 [1, 0.10]                 | this work |
| 8       | 0.76 [1, 0.10]                 | this work |
| 9       | 0.21 [1, 0.09]                 | this work |

[a] Ag/AgCl reference electrodes (ferrocene/ferrocenium couple located at 0.56 V, ΔE = 0.06 V).

Table S5. Linear optical absorption and nonlinear optical absorption cross-section maxima.[a]

| Compound | λ_{max}^{[b]} | σ_2^{[d]} (λ_{max}^{[b]}) | σ_3^{[e]} (λ_{max}^{[b]}) | σ_4^{[f]} (λ_{max}^{[b]}) | Ref. |
|----------|---------------|--------------------------|--------------------------|--------------------------|------|
| 6a       | 413 [9.9]     | 1500 (680)               | 190 (1290)               | -                        | 12   |
|          |               | 1050 (845)               |                          |                          |      |
| 7a       | 412 [12]      | 1490 (650)               | 100 (1240)               | -                        | 12   |
|          |               | 370 (810)                |                          |                          |      |
| 8a       | 403 [11]      | 2500 (670)               | 740 (1290)               | -                        | 12   |
|          | 459 [8.9]     | 1100 (950)               |                          |                          |      |
| 5        | 508 [50]      | 2760 (1150)              | 120 (1650)               | -                        | this work |
|          |               | 1300 (1400)              | 90 (1850)                |                          |      |
| 6        | 439 [29]      | 3250 (1100)              | 1640 (1600)              | 110 (2300)               | this work |
|          | 598 [60]      | 1470 (1350)              | 700 (1800)               |                          |      |
| 7        | 433 [60]      | 16040 (1100)             | 1150 (1600)              | 100 (2260)               | this work |
|          | 601 [102]     |                          | 860 (1800)               |                          |      |
| 8        | 463 [75]      | 13780 (1100)             | 1250 (1750)              | 160 (2260)               | this work |
|          | 583 [114]     |                          | 70 (2380)                |                          |      |
| 9        | 454 [56]      | 27580 (1150)             | 2030 (1730)              | 210 (2100)               | this work |
|          | 616 [86]      | 7700 (1400)              | 810 (1950)               | 70 (2420)                |      |

[a] CH2Cl2. [b] nm. [c] 10^{-4} L mol^{-1} cm^{-1}. [d] GM = 10^{-50} cm^{-4} s photon^{-1}. [e] 10^{-30} cm^{-6} s^2 photon^{-2}. [f] 10^{-110} cm^{-8} s^3 photon^{-3}.
Table S6. Comparison of the molecular weight- and effective-number-of-π-electrons-scaled NLO parameters at local maxima for heptazine compounds.\(^{[a]}\)

| Compound | \(\sigma_2/M\) \(^{[c]}\), \(\sigma_2/N_{\text{eff}}^2\) \(^{[d]}\) \((\lambda_{\text{max}})\) | \(\sigma_3/M\) \(^{[g]}\), \(\sigma_3/N_{\text{eff}}^3\) \(^{[e]}\) \((\lambda_{\text{max}})\) | \(\sigma_4/M\) \(^{[b]}\), \(\sigma_4/N_{\text{eff}}^4\) \(^{[f]}\) \((\lambda_{\text{max}})\) | Ref. |
|----------|-------------------------------------------------|-----------------------------|---------------------------------|------|
| 6a       | 0.46, 3.47 (680)                                 | 0.059, 0.021(1290)          | -                               | 12   |
|          | 0.32, 2.43 (845)                                 |                             |                                 |      |
| 7a       | 0.43, 2.38 (650)                                 | 0.029, 0.0064 (1240)        | -                               | 12   |
|          | 0.11, 0.59 (810)                                 |                             |                                 |      |
| 8a       | 0.70, 4.01 (670)                                 | 0.21, 0.047 (1290)          | -                               | 12   |
|          | 0.31, 1.76 (950)                                 |                             |                                 |      |
| 5        | 3.02, 2.84 (1150)                                | 0.13, 0.0040 (1650)         | -                               | this work |
|          | 1.42, 1.34 (1400)                                | 0.098, 0.0030 (1850)        |                                 |      |
| 6        | 0.99, 7.44 (1100)                                | 0.50, 0.18 (1600)           | 0.034, 0.00058 (2300)           | this work |
|          | 0.45, 3.37 (1350)                                | 0.21, 0.077 (1800)          |                                 |      |
| 7        | 4.63, 25.46 (1100)                               | 0.33, 0.073 (1600)          | 0.029, 0.00025 (2260)           | this work |
|          | 0.25, 0.054 (1800)                               | 0.25, 0.054 (1800)          |                                 |      |
| 8        | 3.83, 21.87 (1100)                               | 0.35, 0.078 (1750)          | 0.044, 0.00040 (2260)           | this work |
|          | 0.19, 0.00018 (2380)                             | 0.019, 0.00018 (2380)       |                                 |      |
| 9        | 7.49, 43.09 (1150)                               | 0.55, 0.12 (1730)           | 0.057, 0.00051 (2100)           | this work |
|          | 2.09, 12.03 (1400)                               | 0.22, 0.050 (1950)          | 0.019, 0.00017 (2420)           |      |

\(^{[a]}\) CH\(_2\)\(_2\)Cl\(_2\) solvent, \(N_{\text{eff}} = 31.2\) (5), 20.9 (6), 25.1 (7, 8), 25.3 (9). \(^{[b]}\) nm. \(^{[c]}\) GM mol g\(^{-1}\). \(^{[d]}\) GM = \(10^{-50}\) cm\(^4\) s photon\(^{-1}\). \(^{[e]}\) \(10^{-80}\) cm\(^8\) s\(^2\) photon\(^{-2}\). \(^{[f]}\) \(10^{-110}\) cm\(^8\) s\(^3\) photon\(^{-3}\). \(^{[g]}\) \(10^{-80}\) cm\(^8\) s\(^2\) photon\(^{-2}\) mol g\(^{-1}\). \(^{[h]}\) \(10^{-110}\) cm\(^8\) s\(^3\) photon\(^{-3}\) mol g\(^{-1}\).
Figure S28. Wavelength dependence of the nonlinear absorption (top) and “effective” cubic NLO coefficients (bottom) of compound 5.
Figure S29. Wavelength dependence of the nonlinear absorption (top) and “effective” cubic NLO coefficients (bottom) of compound 6.
Figure S30. Wavelength dependence of the nonlinear absorption (top) and “effective” cubic NLO coefficients (bottom) of compound 7.
Figure S31. Wavelength dependence of the nonlinear absorption (top) and "effective" cubic NLO coefficients (bottom) of compound 8.
Figure S32. Wavelength dependence of the nonlinear absorption (top) and “effective” cubic NLO coefficients (bottom) of compound 9.
Figure S33. Open-aperture Z-scan data at 1200 nm for a solution of compound 9 in CH₂Cl₂ (black circles) and theoretical curves calculated for $\omega_0 = 25 \, \mu m$ (determined from closed-aperture scans for pure solvent) assuming 2PA (blue line) or 3PA (gray line).

Figure S34. Open-aperture Z-scan data at 1750 nm for a solution of compound 9 in CH₂Cl₂ (black circles) and theoretical curves calculated for $\omega_0 = 31 \, \mu m$ (determined from closed-aperture scans for pure solvent) assuming 2PA (gray line) or 3PA (blue line).
**Figure S35.** Open-aperture Z-scan data at 2470 nm for a solution of compound 9 in CH$_2$Cl$_2$ (black circles) and theoretical curves calculated for $\omega_0 = 35$ µm (determined from closed-aperture scans for pure solvent) assuming 3PA (gray line) or 4PA (blue line).

**Figure S36.** Open-aperture Z-scan data of compound 5 in CH$_2$Cl$_2$ at 800 nm ($\omega_0 = 27$ µm, 35 GW/cm$^2$, 100 data points, Z-scan stage travelled 15 mm in ca. 600 s) and 1800 nm ($\omega_0 = 29$ µm, 255 GW/cm$^2$, 100 data points, Z-scan stage travelled 25 mm in ca. 600 s).
Figure S37. Consecutive scans of compound 5 (in CH₂Cl₂) and compound 9 (in CH₂Cl₂) at 800 nm ($\omega_0 = 27$ µm, 35 GW/cm², 180 s per scan) and 1800 nm ($\omega_0 = 29$ µm, 255 GW/cm², 240 s per scan).
Computational Studies

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) studies were undertaken on models of 5-9. For the sake of computational expediency, model compounds were constructed with phenyl groups in the dppe ligands (PPh$_2$CH$_2$CH$_2$PPh$_2$) and ethyl substituents of the amino groups replaced by H (see Figure S38). Calculated UV-vis data are provided in Table S7. Orbital diagrams of the model compounds are shown in Figures S39-S43.

The DFT/TD-DFT calculations were performed using the Gaussian 16 program package. Geometry optimization of the investigated structures was performed at the B3LYP/6-31G(d)/SDD level of theory in the gas phase. Frequency calculations were carried out at the same level of theory to identify all stationary points as minima (zero imaginary frequencies) and to provide thermal correction to the free energies at 298.15 K and 1 atm. The electronic absorptions of all optimized structures were calculated with B3LYP functionals and D3BJ dispersion correction, and with a polarizable continuum model (PCM) for solvent CH$_2$Cl$_2$. The SDD basis set was used for the transition metal and 6-311G(d,p) basis sets were used for the other atoms. The 20 lowest excitation states were chosen for electronic structure calculations. The 3D isosurface plots of the model compounds were constructed using the Visual Molecular Dynamics program. Multiwfn was used to conduct cube file manipulations.

![Figure S38](image_url) Model compounds used in the computational studies.
Table S7. TD-DFT studies of the model complexes. The first 20 singlet states were calculated. Only transitions with oscillator strengths ($f$) greater than 0.3 are reported. Wavenumbers ($\nu$) are in cm$^{-1}$.

| Complex | State | $\nu$  | $f$   | Major contribution (%) |
|---------|-------|--------|-------|-------------------------|
| 5M      | S$_1$ | 17400  | 1.048 | HOMO $\rightarrow$ LUMO (99) |
|         | S$_2$ | 17400  | 1.046 | HOMO-1 $\rightarrow$ LUMO (99) |
|         | S$_3$ | 22900  | 1.089 | HOMO $\rightarrow$ LUMO+1 (37) |
|         |       |        |       | HOMO-1 $\rightarrow$ LUMO+2 (36) |
|         |       |        |       | HOMO-2 $\rightarrow$ LUMO+1 (17) |
|         | S$_6$ | 22900  | 1.086 | HOMO-1 $\rightarrow$ LUMO+1 (36) |
|         |       |        |       | HOMO $\rightarrow$ LUMO+2 (36) |
|         |       |        |       | HOMO-2 $\rightarrow$ LUMO+2 (18) |
| 6M      | S$_1$ | 17600  | 0.981 | HOMO $\rightarrow$ LUMO (98) |
|         | S$_2$ | 17650  | 0.975 | HOMO-1 $\rightarrow$ LUMO (99) |
|         | S$_8$ | 23500  | 0.789 | HOMO $\rightarrow$ LUMO+2 (45) |
|         |       |        |       | HOMO-1 $\rightarrow$ LUMO+1 (36) |
|         | S$_9$ | 23500  | 0.757 | HOMO-1 $\rightarrow$ LUMO+2 (39) |
|         |       |        |       | HOMO $\rightarrow$ LUMO+1 (38) |
|         |       |        |       | HOMO-2 $\rightarrow$ LUMO+1 (15) |
| 7M      | S$_1$ | 16600  | 0.813 | HOMO $\rightarrow$ LUMO (98) |
|         | S$_2$ | 16600  | 0.811 | HOMO-1 $\rightarrow$ LUMO (98) |
|         | S$_7$ | 22100  | 0.760 | HOMO-6 $\rightarrow$ LUMO (83) |
|         | S$_8$ | 22100  | 0.766 | HOMO-7 $\rightarrow$ LUMO (80) |
|         |       |        |       | HOMO-1 $\rightarrow$ LUMO+1 (5) |
| 8M      | S$_1$ | 17500  | 1.373 | HOMO $\rightarrow$ LUMO (95) |
|         | S$_2$ | 17500  | 1.386 | HOMO-1 $\rightarrow$ LUMO (95) |
|         | S$_{12}$ | 20300 | 0.599 | HOMO-1 $\rightarrow$ LUMO+3 (28) |
|         |       |        |       | HOMO-2 $\rightarrow$ LUMO+2 (18) |
|         |       |        |       | HOMO $\rightarrow$ LUMO+2 (18) |
|         |       |        |       | HOMO-1 $\rightarrow$ LUMO+2 (12) |
|         |       |        |       | HOMO-1 $\rightarrow$ LUMO+1 (10) |
| 9M      | S$_1$ | 14700  | 0.350 | HOMO $\rightarrow$ LUMO (98) |
|         | S$_2$ | 14700  | 0.350 | HOMO-1 $\rightarrow$ LUMO (98) |
|         | S$_4$ | 17150  | 0.400 | HOMO-3 $\rightarrow$ LUMO (97) |
| S_5  | 17150 | 0.400 | HOMO-4 → LUMO (97) |
| S_7  | 20300 | 0.720 | HOMO-6 → LUMO (53) |
|      |       |       | HOMO-2 → LUMO+2 (12) |
|      |       |       | HOMO → LUMO+2 (10) |
|      |       |       | HOMO-1 → LUMO+1 (9) |
| S_8  | 20300 | 0.720 | HOMO-7 → LUMO (53) |
|      |       |       | HOMO-2 → LUMO+1 (14) |
|      |       |       | HOMO → LUMO+1 (8) |
|      |       |       | HOMO-1 → LUMO+2 (8) |
| S_{16}| 22900 | 0.408 | HOMO-5 → LUMO+2 (28) |
|      |       |       | HOMO-3 → LUMO+2 (26) |
|      |       |       | HOMO-4 → LUMO+1 (24) |
|      |       |       | HOMO-5 → LUMO+1 (6) |
|      |       |       | HOMO-4 → LUMO+2 (5) |
| S_{17}| 22900 | 0.408 | HOMO-5 → LUMO+1 (31) |
|      |       |       | HOMO-3 → LUMO+1 (24) |
|      |       |       | HOMO-4 → LUMO+2 (24) |
|      |       |       | HOMO-5 → LUMO+2 (7) |
|      |       |       | HOMO-3 → LUMO+2 (5) |
Figure S39. Molecular orbital diagram of the model compound 5M.
Figure S40. Molecular orbital diagram of the model complex 6M.
Figure S41. Molecular orbital diagram of the model complex 7M.
Figure S42. Molecular orbital diagram of the model complex 8M.
Figure S43. Molecular orbital diagram of the model complex 9M.
Table S8. Intense low-energy absorption features of the model compounds and the corresponding experimental compounds.

| Compound (Model/Experimental) | Calculation | Experiment |
|------------------------------|-------------|------------|
|                              | $\lambda$ (nm) | $\varepsilon \times 10^{5}$ M$^{-1}$ cm$^{-1}$ | $\lambda_{\text{max}}$ (nm) | $\varepsilon \times 10^{5}$ M$^{-1}$ cm$^{-1}$ |
| 5M/5                         | 574         | 1          | 508  | 5 |
|                              | 433         | 1.1        | 355  | 5.9 |
| 6M/6                         | 567         | 1          | 598  | 6 |
|                              | 426         | 0.8        | 439  | 2.9 |
| 7M/7                         | 601         | 0.8        | 601  | 10.2 |
|                              | 448         | 0.7        | 433  | 6 |
| 8M/8                         | 570         | 1.4        | 583  | 11.4 |
|                              | 493         | 0.6        | 463  | 7.5 |
| 9M/9                         | 680         | 0.3        | 616  | 8.6 |
|                              | 582         | 0.4        | 454  | 5.6 |
|                              | 492         | 0.7        |      |    |

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