Electronic Supplementary Information for

A Photoswitchable Supramolecular Complex with Release-and-Report Capabilities

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Content

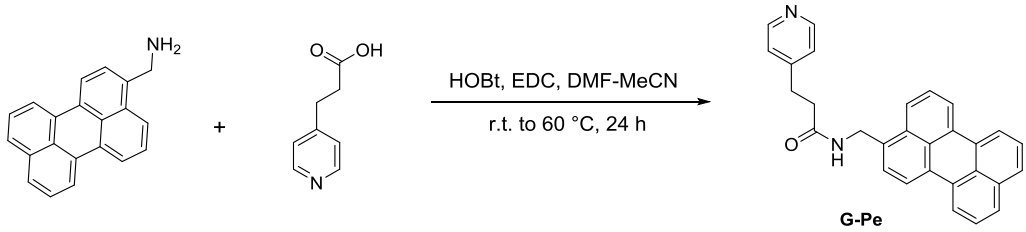
1 Synthesis

Synthesis of the pyridine functionalized DTE derivative, **1**,[1] and the porphyrin dimer, $\mathbf{P_2}$,[2] has been outlined in the literature before. The synthesis of **G-Pe** is described below.

1.1 General methods, materials and instrumentation

^{1}H, ^{13}C, DEPT and gHSQCAD spectra were recorded on an Agilent 400 spectrometer at 298 K. In ^{1}H NMR spectra, chemical shifts (δ/ppm) are referenced to internal reference $(CH_3)_4Si$ (0.00 ppm in $CDCl_3$). In ^{13}C NMR spectra, chemical shifts (δ/ppm) are referenced to the carbon signal of the deuterated solvents (77.20 ppm in $CDCl_3$). Thin-layer chromatography was performed on silica gel plates (Merck Kieselgel 60, F_{254}) to monitor the reactions. Spots were made visible with UV light. Column chromatography was performed with silica gel (Merck silica 60). All chemicals and solvents were purchased from commercial vendors and used as received, unless stated otherwise. Acetonitrile (MeCN) was distilled over CaH_2.

*1.2 Synthesis of N-(perylen-3-ylmethyl)-3-(pyridin-4-yl)propanamide (**G-Pe**)*



Scheme S1. Synthesis of *N*-(perylen-3-ylmethyl)-3-(pyridin-4-yl)propanamide (**G-Pe**).

Anhydrous DMF (1 mL) and distilled MeCN (2 mL) were added to 3-(pyridin-4-yl)propanoic acid (15 mg, 0.1 mmol), 1-ethyl-3-(3'-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (19 mg, 0.1 mmol) and 1-hydroxybenzotriazole (HOBt) (14 mg, 0.1 mmol) in a flask. The mixture was stirred for 30 min at rt. 3-(Aminomethyl)perylene[3] (28 mg, 0.1 mmol) was dissolved in anhydrous DMF (3 mL) and added to the activated acid solution. The reaction mixture was heated at 60 °C for 24 h. The dark-brown solution was concentrated under reduced pressure. Water (20 mL) was added to the residue and the mixture was stirred at rt for 1 h. The precipitate was collected by filtration and washed with water. Purification by flash chromatography [SiO_2; eluents, MeOH/DCM (2:98 → 5:95)] afforded *N*-(perylen-3-ylmethyl)-3-(pyridin-4-yl)propanamide (**G-Pe**) as light yellow solid (33 mg, 80 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (m, 2H; pyridine-ring), 8.24 (d, *J* = 7.2 Hz, 1H; Ar-H), 8.20 (t, *J* = 8.0 Hz, 2H; Ar-H), 8.11 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.74-7.67 (m, 3H; Ar-H), 7.55-7.46 (m, 3H; Ar-H), 7.34 (d, *J* = 7.6 Hz, 1H; Ar-H), 7.13 (m, 2H; pyridine-ring), 5.60 (br s, 1H; NH), 4.81 (t, *J* = 5.2 Hz, 2H; NH*C*H$_2$), 3.03 (t, *J* = 7.4 Hz, 2H; CH_2), 2.53 (d, *J* = 7.4 Hz, 2H; *C*H$_2$CO) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.02 (C_q), 149.99 (2C; CH), 149.97 (C_q), 134.76 (C_q), 132.83 (C_q), 132.79 (C_q), 132.11 (C_q), 131.88 (C_q), 131.17 (C_q), 130.97 (C_q), 129.29 (C_q), 128.57 (C_q), 128.30 (CH), 128.26 (CH), 127.77 (CH), 127.40 (CH), 126.83 (CH), 126.78 (CH), 123.98 (2C; CH), 123.25 (CH), 120.74 (CH), 120.64 (CH), 120.62 (CH), 119.81 (CH), 42.25 (NH*C*H$_2$), 37.03 (CH_2), 30.89 (CH_2) ppm.

1.3 ^{1}H and ^{13}C NMR spectra of ***G-Pe***

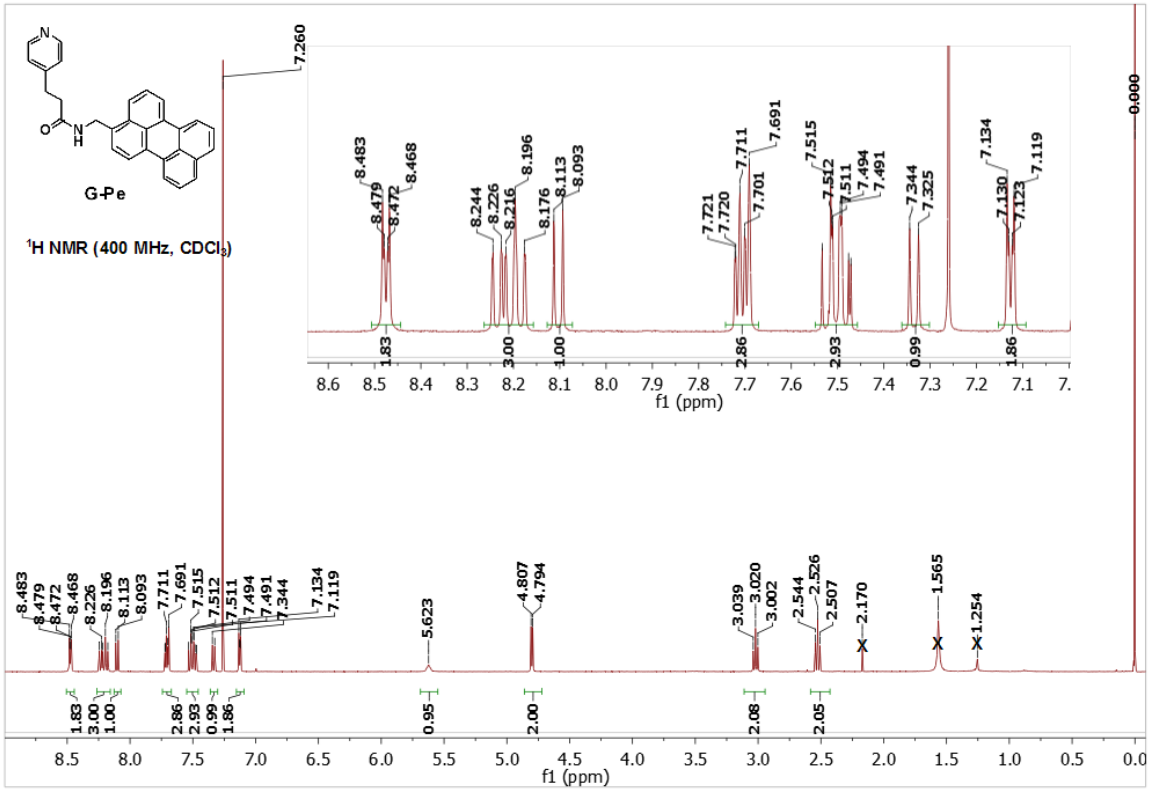


Fig. S1. ^{1}H NMR of **G-Pe.**

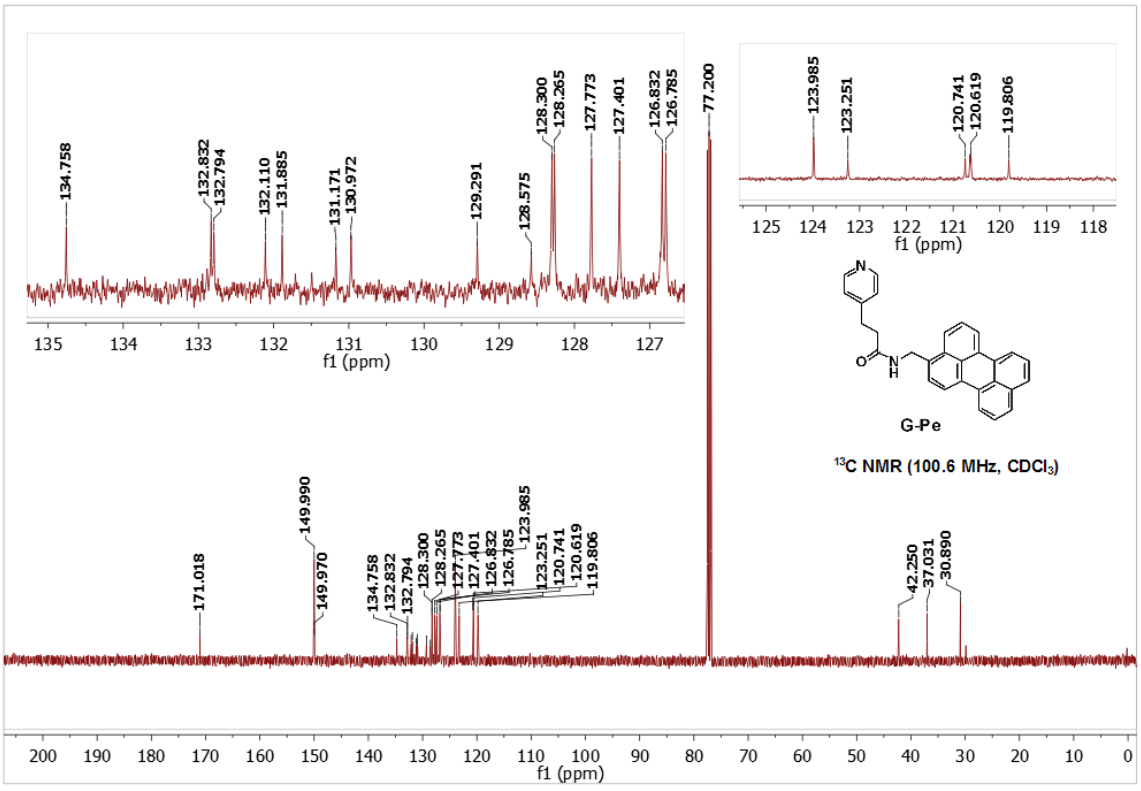


Fig. S2. ^{13}C NMR of **G-Pe.**

2 Spectroscopic Measurements

2.1 General methods, materials and instrumentation

All experiments were performed in toluene. Steady state absorption measurements (photoswitch characterization and $\mathbf{P_2}$ titrations) were carried out in a 1 cm quartz cuvette with a Cary 5000 or Cary 4000 UV/Vis spectrometer. Isomerization quantum yield measurements (see details below) were performed with a Cary 50 Bio UV/Vis spectrometer with a hand held CW SDLaser 301 at 532 nm as light source. For emission experiments (release-and-report), a 1 mm quartz cuvette was used in a SPEX Fluorolog-3 instrument with front-face detection. Photo-induced ring-closing of **1** (**1o** → **1c**) was achieved using 302 nm light generated by a hand-held UVP UV-lamp (model UVM-57, 1.5 mW/cm^2). The corresponding opening reaction (**1c** → **1o**) was achieved with light from a 500 W Hg/Xe-lamp filtered through a 550 nm long-pass filter and a hot-mirror (A = 1.9 at 900 nm). Toluene and 4-aminopyridine (**G**) were purchased from Sigma-Aldrich and used a received.

*2.2 Isomerization quantum yield determination: **1c** → **1o***

For determination of isomerization quantum yield for the DTE opening reaction (**1c** → **1o**) in toluene, the visible light induced decolorization reaction of furylfulgide 2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**FG$_c$** → **FG$_o$**) was used as an actinometric reference reaction.[4] The samples were prepared in a 1 cm quartz cuvette (V = 2.0 mL). Prior to the photo-induced decolorization reaction, the compounds were isomerized to the colored forms and the absorbance at the irradiation wavelength (532 nm) was adjusted to *ca.* 0.05. The decolorization reactions were performed at room temperature with constant stirring and identical irradiation conditions. The decrease in absorption of the colored forms was monitored and fitted to a first order exponential decay function. Comparison of the rate constant, k, for the sample (**1**) to that of the reference (**FG**) allowed for the calculation of the isomerization quantum yield, $\Phi_{1c\rightarrow 1o}$, as

$$\Phi_{\mathbf{1c\rightarrow 1o}} = \frac{k_{\mathbf{1c\rightarrow 1o}}}{k_{FGc\rightarrow FGo}} \times \frac{\varepsilon_{FGc}(532nm)}{\varepsilon_{1c}(532nm)} \times \Phi_{FGc\rightarrow FGo}(532nm)$$

where $\varepsilon_{FGc}(532nm)$ and $\varepsilon_{1c}(532nm)$ are the molar absorption coefficients of **FGc** and **1c**, respectively. The values $\Phi_{FGc\rightarrow FGo}(532nm)$ = 0.051 and $\varepsilon_{ref}(532nm)$ = 6200 M^{-1}cm^{-1} were obtained from the literature.[4d]

*2.3 Steady state absorption spectra of **1** in toluene.*

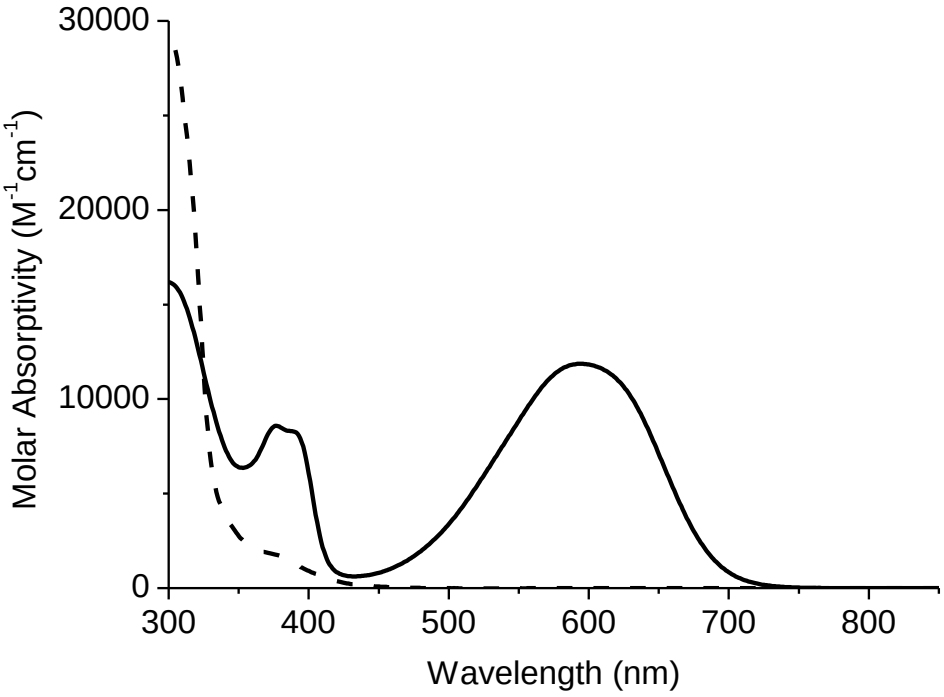


Fig. S3. Absorption spectrum of **1** (72 µM) in toluene; **1o** (dashed line) and **1c** (solid line).

2.4 UV/Vis titrations for binding constants

UV/Vis titrations were performed at room temperature (*ca.* 22° C). In addition to the guest compound (*i.e.* **1o**, **1c**, **G**, or **G-Pe**), the titrant solution also contained the host ($\mathbf{P_2}$) at the same concentration as the receiving host solution, thereby avoiding dilution effects during titration. A single value decomposition (SVD) based fitting procedure[5] was used for extracting the associated binding constants. The spectral region for analysis was chosen to avoid overlapping absorption from the titrant. For **G** and **1o**, displaying no absorption in the visible region, this was not an issue. In the case of **1c**, with substantial absorption in the visible region, the absorption from a reference titration with only **1c** was subtracted from the titration data.

2.4.1 ***1o*** *to* $\mathbf{P_2}$

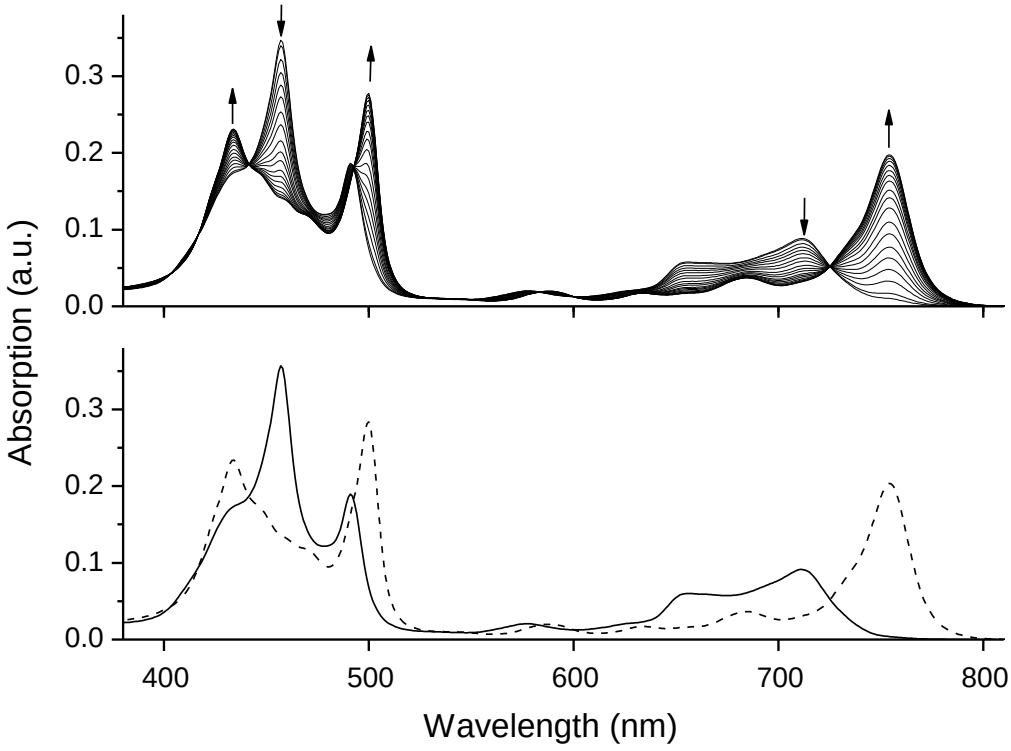


Fig. S4. Top panel: Absorption titration spectra of **1o** to 1μM $\mathbf{P_2}$ for λ = 380-810 nm. Bottom panel: Spectral components extracted in the SVD-analysis; $\mathbf{P_2}$ (solid line) and **1o@**$\mathbf{P_2}$ (dashed line).

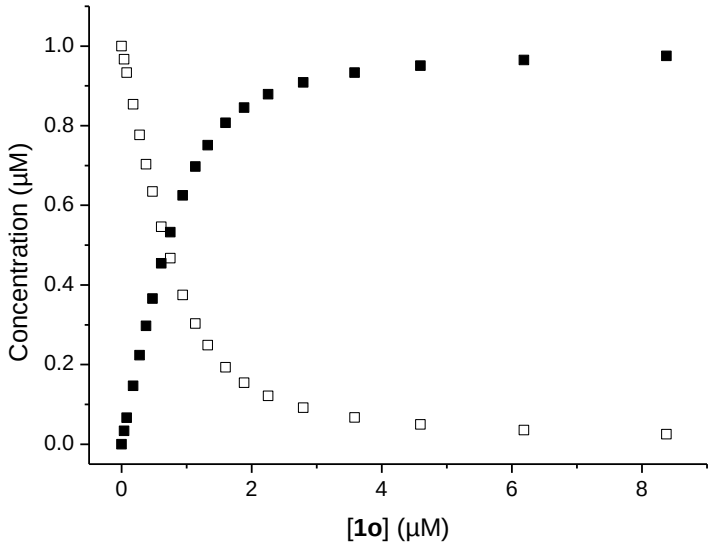


Fig. S5. Concentration profile of the species upon titration of **1o** to 1μM $\mathbf{P_2}$; $\mathbf{P_2}$ (hollow square) and **1o@**$\mathbf{P_2}$ (filled square). The implemented 1:1 binding model yielded a binding constant of $K_a = 5.3 \times 10^6\ M^{-1}$.

2.4.2 ***1c*** *to* $\mathbf{P_2}$

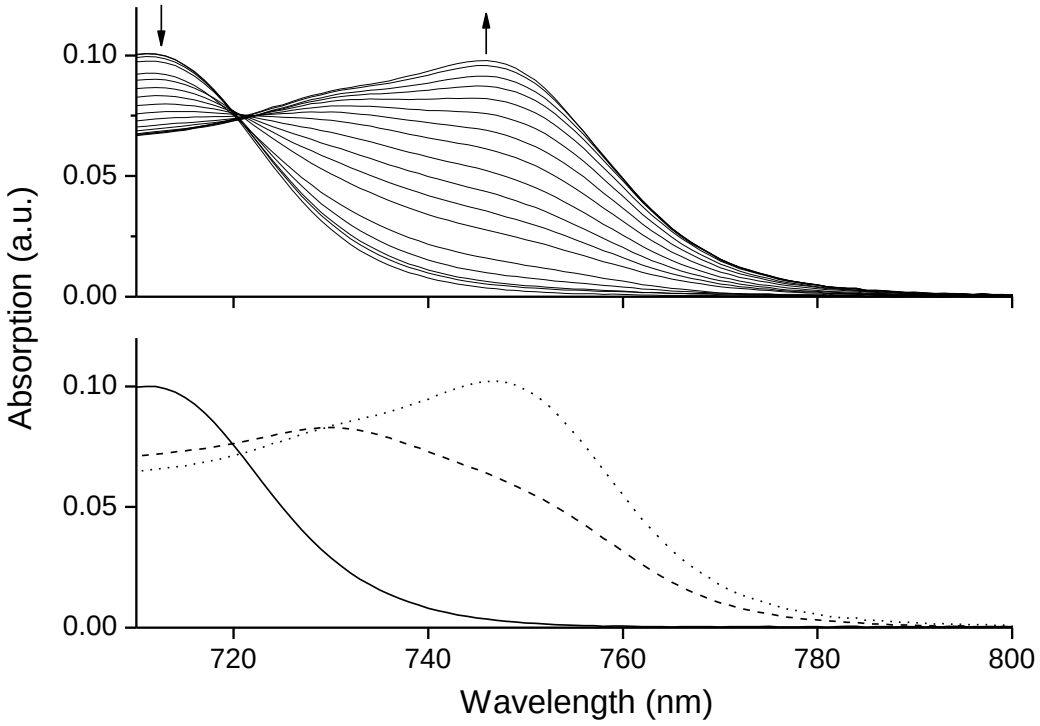


Fig. S6. Top panel: Absorption titration spectra of **1c** to 1μM $\mathbf{P_2}$ for λ = 710-800 nm. Bottom panel: Spectral components extracted in the SVD-analysis; $\mathbf{P_2}$ (solid line) and **1c@**$\mathbf{P_2}$ (dashed line), $(\mathbf{1c})_2$@$\mathbf{P_2}$ (dotted line).

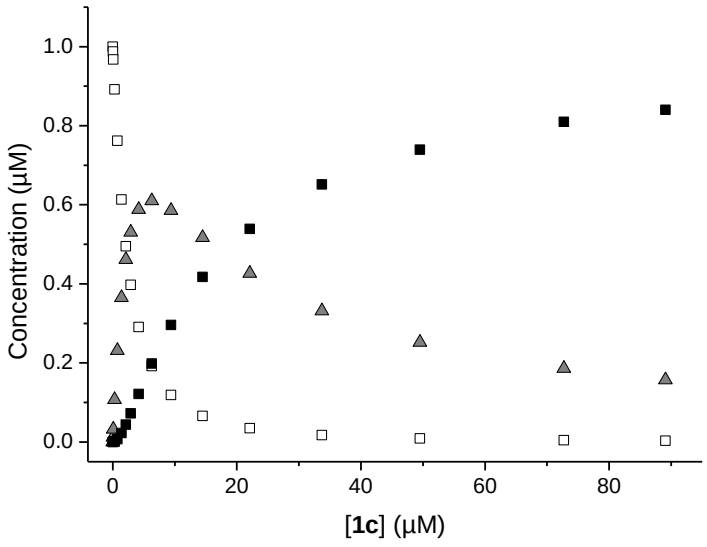


Fig. S7. Concentration profile of the involved species upon titration of **1c** to 1μM $\mathbf{P_2}$; $\mathbf{P_2}$ (hollow square), **1c@**$\mathbf{P_2}$ (gray triangle), and $(\mathbf{1c})_2$**@**$\mathbf{P_2}$ (filled square). The implemented 1:2 binding model yielded binding constants of $K_{a1} = 6.0 \times 10^5\,M^{-1}$ and $K_{a2} = 6.1 \times 10^4\,M^{-1}$.

2.4.3 ***G-Pe*** *to* $\mathbf{P_2}$

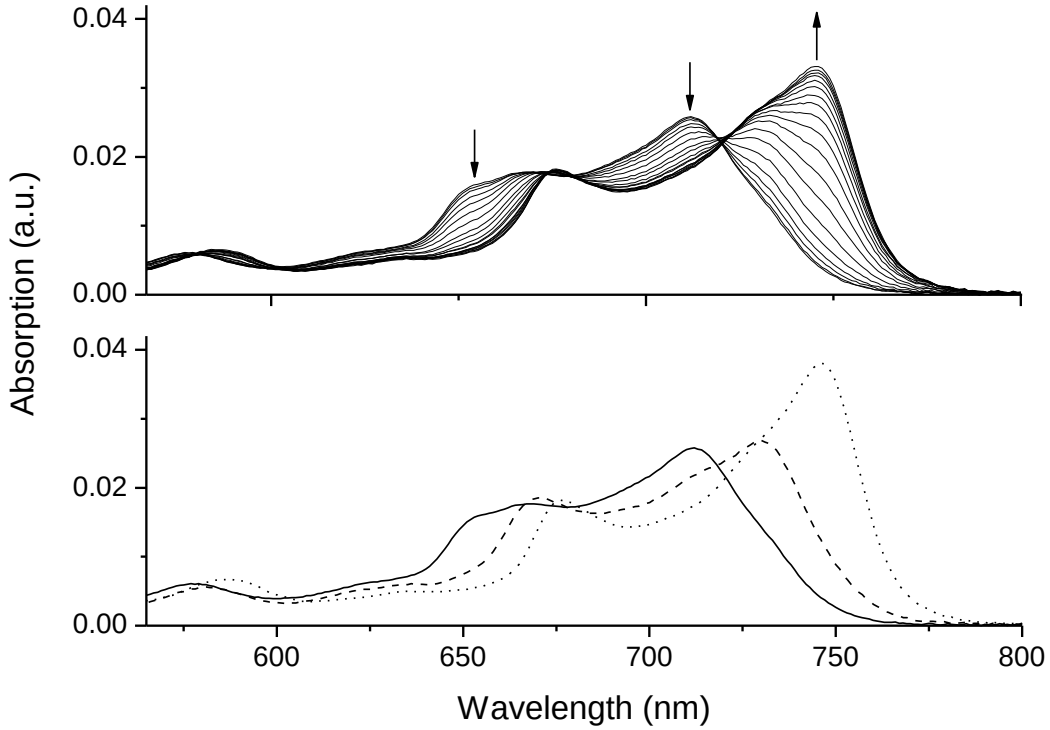


Fig. S8. Top panel: Absorption titration spectra of **G-Pe** to 0.3 μM $\mathbf{P_2}$ for λ = 565-800 nm. Bottom panel: Spectral components extracted in the SVD-analysis; $\mathbf{P_2}$ (solid line) and **G-Pe@**$\mathbf{P_2}$ (dashed line), (**G-Pe)**$_2$@$\mathbf{P_2}$ (dotted line).

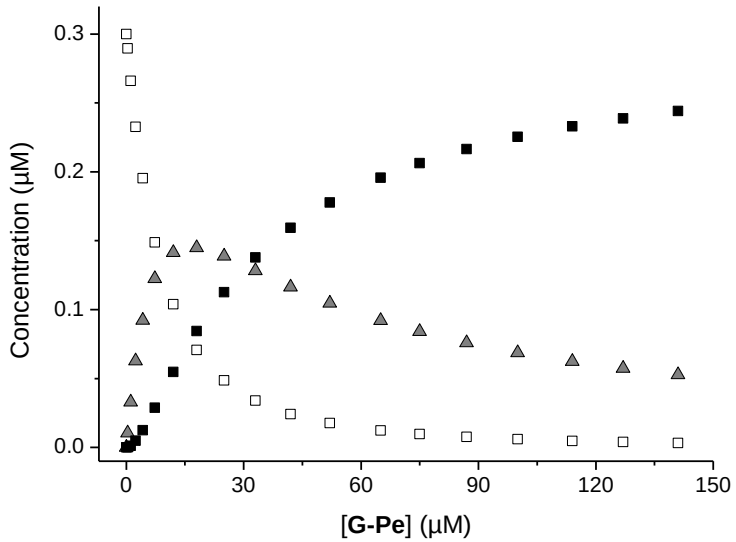


Fig. S9. Concentration profile of the involved species upon titration of **G-Pe** to 1μM $\mathbf{P_2}$; $\mathbf{P_2}$ (hollow square), **G-Pe@**$\mathbf{P_2}$ (gray triangle), and (**G-Pe)**$_2$@$\mathbf{P_2}$ (filled square). The implemented 1:2 binding model yielded binding constants of $K_{a1} = 1.2 \times 10^5\ M^{-1}$ and $K_{a2} = 3.3 \times 10^4\ M^{-1}$.

2.4.4 ***G*** *to* $\mathbf{P_2}$

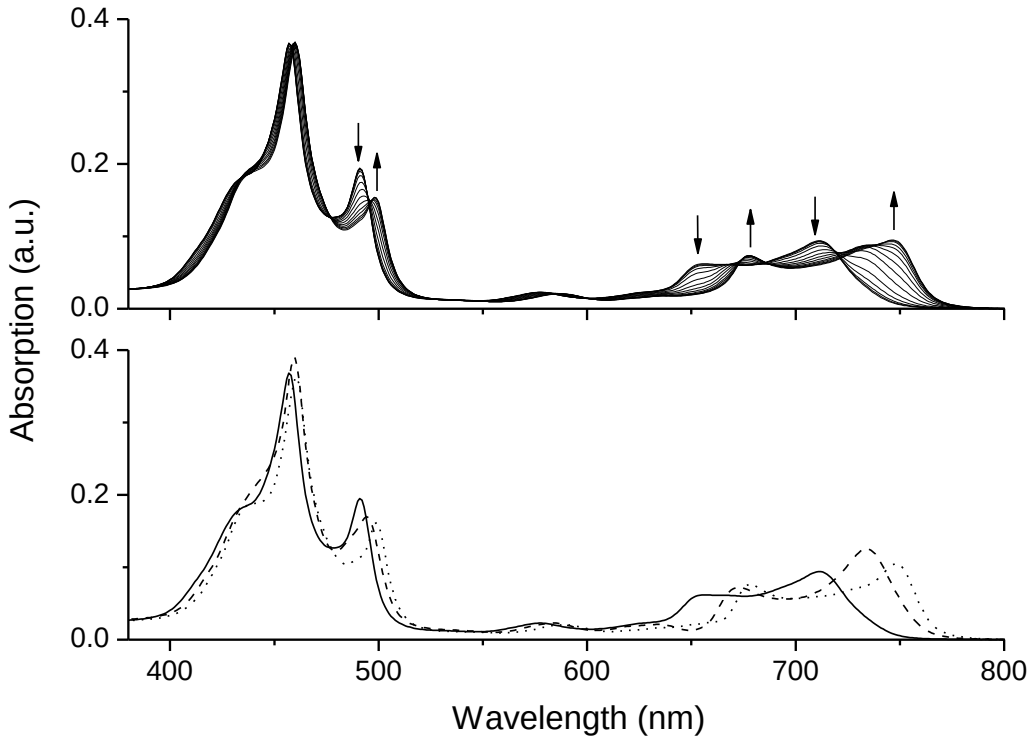


Fig. S10. Top panel: Absorption titration spectra of **G** to 1 μM $\mathbf{P_2}$ for λ = 380-800 nm. Bottom panel: Spectral components extracted in the SVD-analysis; $\mathbf{P_2}$ (solid line) and $\mathbf{G@P_2}$ (dashed line), $\mathbf{G_2@P_2}$ (dotted line).

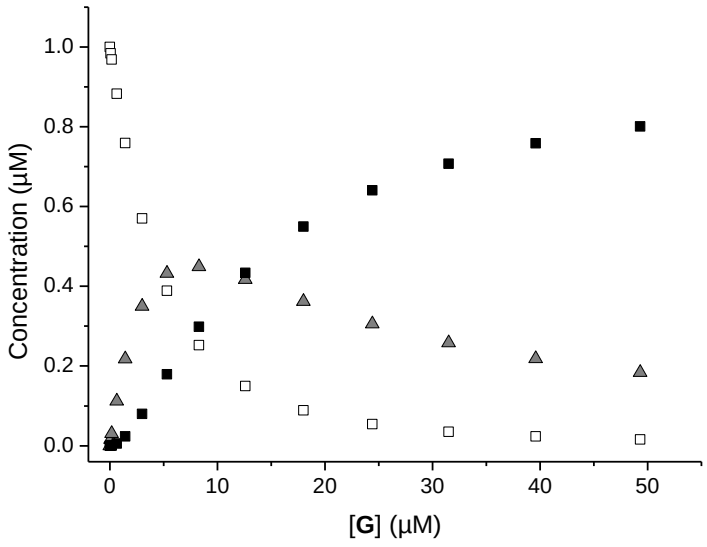


Fig. S11. Concentration profile of the involved species upon titration of **G** to 1μM $\mathbf{P_2}$; $\mathbf{P_2}$ (hollow square), $\mathbf{G@P_2}$ (gray triangle), and $\mathbf{G_2@P_2}$ (filled square). The implemented 1:2 binding model yielded binding constants of $K_{a1} = 2.5 \times 10^5\,M^{-1}$ and $K_{a2} = 9.2 \times 10^4\,M^{-1}$.

*2.5 Coordination-induced quenching of **G-Pe** emission upon addition of **P₂***

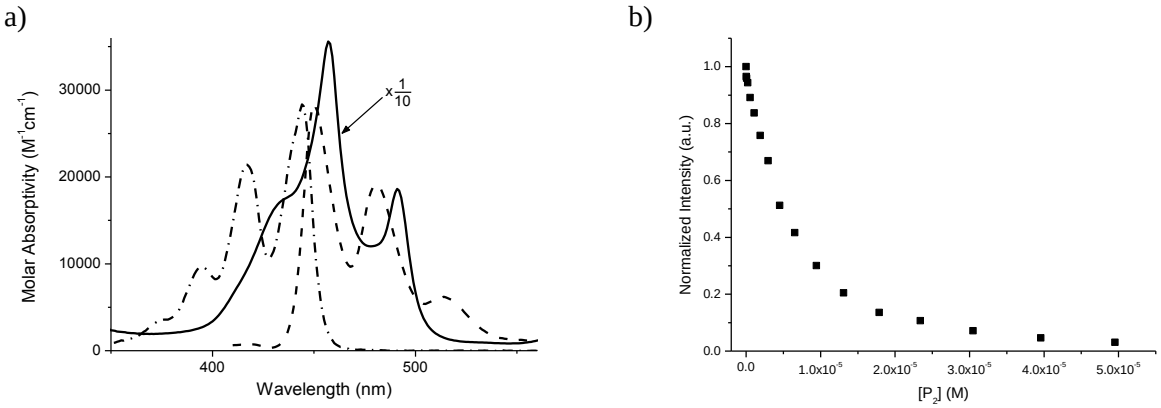


Fig. S12. a) Absorption spectrum of **P₂** (solid) and **G-Pe** (dash-dotted) and normalized emission spectrum of **G-Pe** (dashed). Note that the **P₂** molar absorptivity is scaled by 1/10. b) Normalized **G-Pe** emission upon **P₂** addition. It is clearly seen that coordination to **P₂** quenches the **G-Pe** emission. These results are in accord with the observed binding constants for **G-Pe** to **P₂** binding (see titration above), in combination with the calculated Förster distance, R_0 = 66 Å.

3 References

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