Controlling Intramolecular Förster Resonance Energy Transfer and Singlet Fission in a Subporphyrazine–Pentacene Conjugate by Solvent Polarity

David Guzmán*, Ilias Papadopoulos*, Giulia Lavarda, Parisa R. Rami, Rik R. Tykwinski,*, M. Salomé Rodríguez-Morgade,*, Dirk M. Guldi,*, and Tomás Torres*

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General Procedures, Materials and Methods

Synthesis and characterization

Abbreviations (*Synthesis and characterization*). CuTC = copper (I) thiophene-2-carboxylate; DCM = dichloromethane; DCTB = trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile; DMAP = 4-dimethylaminopyridine; DMI = 1,3-dimethyl-2-imidazolidinone; EDC = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; EtOAc = ethyl acetate; FT-IR = Fourier-transform infrared spectroscopy; HRMS = high resolution mass spectrometry; MALDI-TOF = matrix-assisted laser desorption/ionization - time of flight; MS = mass spectrometry; NMR = nuclear magnetic resonance; Pnc2 = pentacene dimer; PPG = polypropylene glycol; ppm = part per million; SubPz = subporphyrazine; TLC = thin layer chromatography.

**Syntheses and Purifications.** All manipulations were carried out under an argon atmosphere using conventional Schlenk techniques. Pnc2COOH,[1] bis(propylthio)maleonitrile,[2] and CuTC[3] were prepared following reported procedures. The rest of chemicals were purchased from commercial suppliers and used without further purification. “Synthetic grade” solvents were used for chemical reactions, column chromatography purifications, and “anhydrous grade” for reactions under dry conditions. Additionally, some solvents were further dried by distillation with sodium/benzophenone [tetrahydrofuran (THF)] or with a solvent purifying system by Innovative Technology Inc. MD-4-PS. Solid, hygroscopic reagents were dried in a vacuum oven before use. Column chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60 Å) and TLC was performed on aluminum sheets pre-coated with silica gel 60 F254 (Merck). Size exclusion chromatography was performed on Bio-Beads™ S-X1 Support (200-400 mesh).

**Instrumental Analyses.** 1H NMR and 13C NMR spectra were obtained using a Bruker Advance 400 (400 MHz) spectrometer. The temperature was actively controlled at 298 K, unless indicated otherwise. Chemical shifts are measured in ppm relative to tetramethylsilane (TMS). Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) MS and high-resolution mass spectrometry (HRMS) spectra were recorded with a BRUKER ULTRAFLEX III instrument equipped with a nitrogen laser operating at 337 nm. A convenient matrix of DCTB was used for the measurements of the SubPz derivatives. Infrared (FT-IR) spectra were recorded on a
Bruker Alpha II spectrometer by attenuated total reflection (ATR) technic, in all cases solid samples. Previous UV/Vis ($\lambda_{\text{max}}$ and $\varepsilon$) and fluorescence spectra were recorded with a JASCO V-660-spectrophotometer and with a JASCO V8600-spectrofluorometer, respectively.

**Photophysics**

**Steady-State Absorption and Fluorescence.** Steady-state absorption experiments were performed on a Perkin Elmer Lambda 2 spectrometer at room temperature (rt). Steady-state fluorescence experiments were carried out on a FluoroMax3 spectrometer from Horiba in the visible detection range at rt. The data was recorded using Fluorescence software from Horiba Jobin Yvon. The fluorescence quantum yields ($\Phi_F$) were obtained by means of gradient analyses using Nile blue a ($\Phi_F = 0.27$) in methanol for the SubPz centered fluorescence and zinc phthalocyanine ($\Phi_F = 0.30$) in toluene for the Pnc$_2$ centered fluorescence. All measurements were performed in 10 x 10 mm quartz cuvettes at rt.

**Time-Correlated Single Photon Counting (TCSPC).** Fluorescence lifetimes were recorded via the TCPSC setup using a FluoroLog3 emission spectrometer, from Horiba JobinYvon, equipped with an R3809U-58 MCP, from Hamamatsu, and an EXW-6 (NKT) SuperK Extreme high power supercontinuum fiber laser with excitation wavelengths at 480 and 633 nm (~150 ps fwhm) for the SubPz and Pnc$_2$ centered fluorescence, respectively.

**Femto- (fsTA) and Nanosecond (nsTA) Transient Absorption Spectroscopy.** FsTA (0 to 5250 ps) and nsTA (1 ns to 400 $\mu$s) measurements were carried out with an amplified Ti:sapphire CPA-2110 fs laser system (Clark MXR: output 775 nm, 1 kHz, 150 fs pulse width) using the HELIOS and EOS transient absorption pump/probe detection systems from Ultrafast Systems. Solutions were purged with argon for ~15 minutes in 2 x 10 mm cuvettes. The 480 and 633 nm excitation wavelengths, with respective energies of 400 nJ, were generated via a noncolinear optical parametric amplifier from Clark MXR (NOPA). TA spectra were obtained by the same HELIOS and EOS detection systems. In order to ensure a homogenous excitation of the probed area, the spot diameter of the pump beam was kept always larger than that of the probe beam. The delays of the probe pulses were controlled by a delay stage, for fsTA, or electronic response, for nsTA, with respect to the pump pulses, respectively. A beam splitter split the probe pulses into a signal and reference beam, before passing the sample. In order
to correct for fluctuations in the probe beam intensity, the probe and reference beam were
detected independently. Furthermore the spectra were acquired shot-by-shot and averaged
at each delay over ~1500 times, to ensure a reasonable signal-to-noise ratio.

**FsTA and NsTA Data Evaluation.** Results from fsTa and nsTA data have been analyzed via
multiwavelength and GloTarAn target analysis. Target analysis was performed on the TA data
sets using the proposed sequential model. The analytical solution to the coupled differential
equations that describe the kinetic model is convoluted with a Gaussian instrument response
function. After the least-squares fitting has converged, the raw data matrix is deconvoluted
using the specific solution to the kinetic model and parameters from the fit to obtain the
species-associated spectra (SAS) and their populations as a function of time. GloTarAn is a
Java-based graphical user interface to the R-package TIMP, which was developed for global
and target analysis of time-resolved spectroscopy data. The dispersion (chirp of the white-
light pulse) of the instrument response function (IRF) was modeled, via Surface Xplorer by
Ultrafast Systems, and taken into account during the fitting procedure.

**Triplet Quantum Yield (TQY) Determination.** The determination of the TQY followed the same
procedure as in our previous works.\(^4,5\) In brief summary, the TQY was obtained by following
the intensification of the ground state bleach (GSB) relating to Pnc\(_2\). The SAS were corrected,
in order to account for residual SubPz centered contributions (e.g. GSB, fluorescence) of the
Pnc\(_2\) centered GSB. Equation (1) was used for the TQY calculation of the Pnc\(_2\)COOH reference
compound:

\[
\frac{\Delta OD_{SAS}(^1(T_1T_1)_{Pnc_2})}{\Delta OD_{SAS}(^1(S_1S_0)_{Pnc_2})} \times 100\% = TQY
\]

While equation (2) was used for the TQY calculation of the SubPzPnc\(_2\) conjugate:

\[
\frac{\Delta OD_{SAS}(^1(T_1T_1)_{Pnc_2})^{CT}(S_1S_0)_{Pnc_2}}{\Delta OD_{SAS}(^1(S_1S_0)_{Pnc_2})^{CT}(S_1S_0)_{Pnc_2}} \times 100\% = TQY
\]

Here \(\Delta OD_{SAS}(^{CT}(S_1S_0)_{Pnc_2})\) rather than \(\Delta OD_{SAS}(^1(S_1S_0)_{Pnc_2})\) was utilized, as the singlet excited
state of SubPzOH \(^1(S_1)_{SubPzOH}\) featured a positive transient in the area of the GSB of Pnc\(_2\),
therefore distorting the intensity of the GSB relating to \(^1(S_1S_0)_{Pnc_2}\).
**FRET Rate Constant Determination.** The determination of the FRET rate also followed the same procedure from previous works\(^4,^5\) using the following equations (3)-(7):

\[
R = R_0 \left( \frac{1 - E}{E} \right)^{\frac{1}{6}} \tag{3}
\]

\(R\) = FRET distance; \(R_0\) = critical energy donor-acceptor distance; \(E\) = FRET efficiency.

\[
E = 1 - \frac{\tau_{DA}}{\tau_D} \tag{4}
\]

\(E\) = FRET efficiency; \(\tau_{DA}\) = experimental lifetime (TA) of energy donor-acceptor conjugate; \(\tau_D\) = experimental fluorescence lifetime of energy donor (TCSPC).

\[
R_0 = 0.2108 \left( \kappa^2 \Phi_F n^{-4} J \right)^{\frac{1}{6}} \tag{5}
\]

\(R_0\) = critical energy donor-acceptor distance; \(\kappa^2\) = orientation factor; \(n\) = refractive index of the solvent; \(J\) = degree of spectral overlap.

\[
J = \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \tag{6}
\]

\(J\) = degree of spectral overlap; \(F_D\) = fluorescence intensity of the donor at wavelength \(\lambda\).

The fluorescence spectra have to be normalized to fulfill equation (7); \(\varepsilon_A\) = extinction coefficient of the acceptor at wavelength \(\lambda\)

\[
\int_0^\infty F_D(\lambda) d\lambda = 1 \tag{7}
\]

The detailed procedure (including a description of a software-based algorithm to calculate the spectral overlap integral \(J\)) is described by Hink et al.\(^6\) For \(\kappa^2\) we used \(2/3\) (~0.67),\(^7\) as often used for non-rigid systems (“dynamic isotropic limit”).\(^8\) The refractive indices \(n\) were taken as 1.506,\(^9\) 1.496,\(^10\) 1.518,\(^11\) and 1.529\(^9\) for xylene, toluene, anisole, and benzonitrile, respectively. See Table 3 for a summary of the parameters used for the FRET rate constant calculation as well as for an overview of the obtained values for the FRET constants.
**Synthesis and Characterization**

**Scheme S1.** Synthetic route and detailed steps for the preparation of SubPzOH and SubPzPnc₂ conjugate.
An oven-dried two-neck round-bottom flask connected to a condenser and held under an argon atmosphere was charged with bis(propylthio)maleonitrile (452.0 mg, 2.00 mmol). A 1.0 M solution of BCl$_3$ in p-xylene (2.0 mL, 2.00 mmol) was then added into the flask via a syringe, and the mixture was heated at 110 °C for 1 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The resulting dark violet crude was dissolved in anhydrous toluene (4 mL) and 4-hydroxybenzaldehyde (1.50 g, 12.30 mmol) was added. The mixture was stirred to reflux for 2 h under an argon atmosphere followed by removal of the solvent under reduced pressure once more. The black crude material was passed through a short pad of compressed Celite using a 9:1 mixture of n-hexane/ethyl acetate, followed by the column chromatography on silica gel (20:1 mixture of n-hexane/ethyl acetate), collecting the two red fractions close to each other. The red viscous solid obtained was dissolved in 25 mL of anhydrous DMI at 0 °C under an argon atmosphere. Then, 1-propanethiol (36 μL, 0.40 mmol, 0.2 equiv respect to bis(propylthio)maleonitrile) and freshly distilled triethylamine (56 μL, 0.40 mmol, 0.2 equiv respect to bis(propylthio)maleonitrile) were added via the syringe, and the resulting mixture was stirred heating from 0 °C to room temperature for 1 h. Once the reaction is completed (TLC showed just one red spot in n-hexane/ethyl acetate 20:1) the product was extracted with diethyl ether and washed three times with water, dried over MgSO$_4$, and the solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel (7:3 mixture of n-hexane/ethyl acetate) giving pure target compound 1 (65.0 mg, 12%) as a red viscous solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 9.69 (s, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 5.43 (d, $J = 8.0$ Hz, 2H), 4.08–4.01 (m, 6H), 3.65–3.58 (m, 6H), 2.05–1.87 (m, 12H), 1.17 (t, $J = 7.2$ Hz, 18H).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 190.6, 158.8, 154.1, 132.0, 131.1, 130.2, 119.4, 36.9, 23.7, 13.5.
**FT-IR** (ATR): $\nu$ (cm$^{-1}$) = 2961, 2929, 2870, 2727, 1695, 1597, 1573, 1477, 1450, 1287, 1235, 1172, 1119, 1001 (S), 895, 838, 749, 579.

**UV/Vis** (CHCl$_3$) $\lambda_{\text{max}}$ (nm) ($\log \varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 280 (4.7), 442 (4.6), 558 (4.5).

**Fluorescence** (CHCl$_3$): $\lambda_{\text{em}}$ = 525 nm; $\lambda_{\text{em}}$ = 680 nm.

**MS** (MALDI-TOF, DCTB, +): $m/z$ = 810.2 [M]$^+$; 689.1 [M – Axial ligand]$^+$

**HRMS** (MALDI-TOF): Calculated for [M]$^+$ C$_{37}$H$_{47}$BN$_6$O$_2$S$_6$ 809.2209; found 809.2253.

**Figure S1.** $^1$H NMR (400 MHz) spectrum of 1 in CDCl$_3$ at 298 K.
Figure S2. $^1$H NMR spectrum of 1, detail of the region between 4.3 ppm and 1.7 ppm.
Figure S3. $^{13}$C NMR (100.6 MHz) spectrum of 1 in CDCl$_3$ at 298 K.
Figure S4. MALDI-TOF mass spectrum (in DCTB matrix) of 1.
Figure S5. Upper part – HRMS (MALDI-TOF) spectrum (in DCTB+PPGNa 790 matrix) of 1. Lower part – Calculated isotopic pattern of 1.
Figure S6. FT-IR spectrum (ATR) of 1.
Figure S7. UV/Vis absorption (solid line) and normalized fluorescence (dashed line) spectra of 1 in chloroform.
An oven-dried 10 mL Schlenk was over-dried and purged with argon during 10 min. Subsequently, hexa(propylthio)-subporphyrazine 1 (47.0 mg, 58.95 μmol), 3,4,5-trimethoxyphenylboronic acid (221.0 mg, 1.04 mmol), [Pd(PPh₃)₄] (40.9 mg, 35.37 μmol, 60 mol %), and CuTC (198.0 mg, 1.04 mmol) were added into the Schlenk and purged with argon for 10 min, followed by the addition of anhydrous THF (5 mL) via cannula. The reaction mixture was stirred at 60 ºC for 18 h under an argon atmosphere. Then, the mixture was cooled to room temperature and passed through a short silica gel column using THF as eluent. The solvent was removed and the residue was purified by silica gel column chromatography (mixture of n-hexane/ethyl acetate/THF 4 : 5.6 :0.4). The product 2 was obtained as a purple solid (28.5 mg, 36%).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 9.68 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.15 (s, 12H), 5.55 (d, J = 8.0 Hz, 2H), 3.92 (s, 18H), 3.62 (s, 36H).

**¹³C NMR** (100.6 MHz, CDCl₃): δ (ppm) = 190.6, 159.1, 156.8, 153.2, 138.7, 133.3, 132.0, 131.9, 131.5, 129.8, 128.5, 128.4, 126.7, 118.4, 108.6, 61.0, 56.0.
Figure S8. $^1$H NMR (400 MHz) spectrum of 2 in CDCl$_3$ at 298 K.
Figure S9. $^{13}$C NMR (100.6 MHz) spectrum of 2 in CDCl$_3$ at 298 K.
4-(Hydroxymethyl)phenoxy[2,3,7,8,12,13-hexa(3'',4'',5''-trimethoxyphenyl)]subporphyrinato]boron(III) (SubPzOH)

In an oven-dried 5 mL round-bottom Schlenk was charged with formyl-SubPz \textbf{2} (17.8 mg, 13.06 μmol), NaBH$_4$ (1.0 mg, 26.12 μmol) and anhydrous DCM (3 mL) under argon atmosphere. The solution was stirred at 0 °C for 5 min in the dark, then MeOH (1.5 mL) was added dropwise. The resulting reaction mixture was stirred for 15 min at 0 °C, and quenched by the addition of water (5 mL). The product was extracted with ethyl acetate, washed with brine, and dried over anhydrous MgSO$_4$. After filtration and evaporation, the solid residue was purified by silica gel column chromatography (mixture of n-hexane/ethyl acetate/THF 4 : 5.6 : 0.4) giving pure compound \textbf{SubPzOH} (13.5 mg, 76%) as a garnet solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.14 (s, 12H), 6.88 (d, $J = 8.0$ Hz, 2H), 5.50 (d, $J = 8.0$ Hz, 2H), 4.42 (s, 2H), 3.91 (s, 18H), 3.62 (s, 36H).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$(ppm) = 156.8, 153.2, 152.7, 138.6, 133.3, 133.1, 128.2, 126.9, 118.5, 108.6, 64.8, 61.0, 56.0.

FT-IR (ATR): $\nu$ (cm$^{-1}$) = 3529, 2998, 2926, 2853, 1738, 1672, 1579, 1510, 1477, 1450, 1287, 1235, 1125 (S), 1008, 923, 870, 843, 717.

UV/Vis (CHCl$_3$) $\lambda_{max}$ (nm) (log ε/dm$^3$ mol$^{-1}$ cm$^{-1}$): 282 (4.8), 446 (4.6), 557 (4.7).

Fluorescence (CHCl$_3$): $\lambda_{ex}$ = 500 nm; $\lambda_{em}$ = 672 nm.

MS (MALDI-TOF, DCTB, +): $m/z$ = 1365.5 [M]$^+$; 1241.5 [M – Axial ligand]$^+$

HRMS (MALDI-TOF): Calculated for [M]$^+$ C$_{73}$H$_{73}$BN$_6$O$_{20}$ 1363.5004; found 1363.4943.
Figure S10. $^1$H NMR (400 MHz) spectrum of SubPzOH in CDCl$_3$ at 298 K.
Figure S11. $^{13}$C NMR (100.6 MHz) spectrum of SubPzOH in CDCl$_3$ at 298 K.
Figure S12. MALDI-TOF mass spectrum (in DCTB matrix) of SubPzOH.
Figure S13. Upper part – HRMS (MALDI-TOF) spectrum (in DCTB + PPGNa 1000 + PPGNa 2000 matrix) of SubPzOH. Lower part – Calculated isotopic pattern of SubPzOH.
Figure S14. FT-IR spectrum (ATR) of SubPzOH.
**Figure S15.** UV/Vis absorption (solid line) and normalized fluorescence (dashed line) spectra of SubPzOH in chloroform.
To a solution of SubPzOH (8.0 mg, 5.86 μmol), Pnc₃COOH (21.0 mg, 19.40 μmol), and DMAP (0.4 mg, 3.27 μmol) in deoxygenated THF (2 mL), EDC (4.0 mg, 26.00 μmol) was one-portion added under argon atmosphere at 0 ºC. The resulting reaction mixture was stirred at 0 ºC for 1 h, then the mixture was allowed to reach room temperature and kept under stirring overnight. Once the reaction is completed (monitored by TLC), the solvent was evaporated under reduced pressure, and the residue was passed through a short-pad of silica gel using a mixture of n-hexane/AcOEt/THF (2:6:2) as eluent. Then, the solvent was evaporated and the residue was purified by size-exclusion column chromatography on Bio-BeadsTM S-X1 (200-400 mesh) using chloroform as the eluent, to give the target material as a dark violet solid (2.8 mg, 20%).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 9.31 (s, 4H), 9.25 (s, 4H), 8.51 (s, 3H), 8.03 (d, J = 8.0 Hz, 4H), 7.97 (d, J = 8.0 Hz, 4H), 7.44 – 7.35 (m, 8H), 7.13 (d, J = 8.0 Hz, 2H), 7.12 (s, 12H), 5.58 (d, J = 8.0 Hz, 2H), 5.29 (s, 2H), 3.88 (s, 18H), 3.57 (s, 36H), 1.43 – 1.39 (m, 42H).

**¹³C NMR** (100.6 MHz, CDCl₃): δ (ppm) = 156.9, 153.2, 138.6, 133.1, 132.3, 130.5, 130.3, 129.8, 128.7, 128.6, 126.8, 126.3, 126.2, 108.6, 61.0, 55.9, 19.0, 11.7.

**FT-IR** (ATR): ν (cm⁻¹) = 2930, 2860, 2128, 1726, 1580, 1510, 1461, 1390, 1313, 1240, 1177, 1126 (S), 1011, 875, 842, 768, 737, 674, 588, 460.

**UV/Vis** (CHCl₃) λ_max (nm) (log ε/dm³ mol⁻¹ cm⁻¹): 351 (4.7), 372 (4.7), 440 (4.6), 558 (4.7), 602 (4.5), 660 (4.7).

**Fluorescence** (CHCl₃): λ_ex = 540 nm; λ_em = 674 nm.

**MS** (MALDI-TOF, DCTB, +): m/z = 2430.0 [M⁺]

**HRMS** (MALDI-TOF): Calculated for [M⁺] C₁₅₀H₁₄₁BN₆O₂₂Si₂ 2427.9812; found 2427.9797.
Figure S16. $^1$H NMR (400 MHz) spectrum of SubPzPnc$_2$ conjugate in CDCl$_3$ at 298 K.
Figure S17. $^1$H NMR spectrum of SubPzPnc$_2$. Expansion of the region between 9.4 ppm and 7.3 ppm ($^1$H aromatic pentacene dimer).
**Figure S18.** $^{13}$C NMR (100.6 MHz) spectrum of SubPzPnc$_2$ in CDCl$_3$ at 298 K.
Figure S19. MALDI-TOF mass spectrum (in DCTB matrix) of **SubPzPnc<sub>2</sub>**.
Figure S20. Upper part – HRMS (MALDI-TOF) spectrum (in DCTB + PPGNa 2000 + PPGNa 2700 matrix) of SubPzPnc₂. Lower part – Calculated isotopic pattern of SubPzPnc₂.
Figure S21. FT-IR spectrum (ATR) of \textit{SubPzPnc}_2.
Figure S22. UV/Vis absorption (solid line) and normalized fluorescence (dashed line) spectra of SubPzPnc$_2$ in chloroform.
Photophysics

Figure S23. Absorption spectra of $\text{Pnc}_2\text{COOH}$ (black), $\text{SubPzOH}$ (red), and $\text{SubPzPnc}_2$ (blue) in xylene (Xyl).
Figure S24. a) Absorption spectra of Pnc\textsubscript{2}COOH (black), SubPzOH (red), and SubPzPnc\textsubscript{2} (blue) in toluene. b) Normalized absorption spectra of Pnc\textsubscript{2}COOH (black), SubPzOH (red), and SubPzPnc\textsubscript{2} (blue) in toluene. c) Normalized fluorescence spectra of SubPzOH (red), Pnc\textsubscript{2}COOH (black), and SubPzPnc\textsubscript{2} (blue) in toluene. Normalization in (a): The Pnc\textsubscript{2}COOH centered absorption (∼660 nm) was used as a point of normalization for Pnc\textsubscript{2}COOH and SubPzPnc\textsubscript{2}, whereat the intensity of the SubPzOH centered maximum (∼560 nm) was compared to SubPzPnc\textsubscript{2}. Normalization in (b): The Pnc\textsubscript{2}COOH centered fluorescence (∼666 nm) was used as a point of normalization, thus highlighting the comparatively lower Φ\textsubscript{F} of SubPzOH and SubPzPnc\textsubscript{2}. 
Figure S25. a) Absorption spectra of Pnc\textsubscript{2}COOH (black), SubPzOH (red), and SubPzPnc\textsubscript{2} (blue) in anisole. b) Normalized absorption spectra of Pnc\textsubscript{2}COOH (black), SubPzOH (red), and SubPzPnc\textsubscript{2} (blue) in anisole. c) Normalized fluorescence spectra of SubPzOH (red), Pnc\textsubscript{2}COOH (black), and SubPzPnc\textsubscript{2} (blue) in anisole. Normalization in (a): The Pnc\textsubscript{2}COOH centered absorption (\textasciitilde 660 nm) was used as a point of normalization for Pnc\textsubscript{2}COOH and SubPzPnc\textsubscript{2}, whereat the intensity of the SubPzOH centered maximum (\textasciitilde 560 nm) was compared to SubPzPnc\textsubscript{2}. Normalization in (b): The Pnc\textsubscript{2}COOH centered fluorescence (\textasciitilde 670 nm) was used as a point of normalization, thus highlighting the comparatively lower \( \Phi_F \) of SubPzOH and SubPzPnc\textsubscript{2}. 
Figure S26. a) Absorption spectra of Pnc$_2$COOH (black), SubPzOH (red), and SubPzPnc$_2$ (blue) in benzonitrile. b) Normalized absorption spectra of Pnc$_2$COOH (black), SubPzOH (red), and SubPzPnc$_2$ (blue) in benzonitrile. c) Normalized fluorescence spectra of SubPzOH (red), Pnc$_2$COOH (black), and SubPzPnc$_2$ (blue) in benzonitrile. Normalization in (a): The Pnc$_2$COOH centered absorption (~666 nm) was used as a point of normalization for Pnc$_2$COOH and SubPzPnc$_2$, whereat the intensity of the SubPzOH centered maximum (~560 nm) was compared to SubPzPnc$_2$. Normalization in (b): The Pnc$_2$COOH centered fluorescence (~674 nm) was used as a point of normalization, thus highlighting the comparatively lower $\Phi_F$ of SubPzOH and SubPzPnc$_2$. 
Table S1. Photophysical parameters of \textbf{Pnc$_2$COOH}, \textbf{SubPzOH}, and \textbf{SubPzPnc$_2$} in toluene, anisole and benzonitrile.

| Solvent     | Compound       | \(\lambda_{abs} / \text{nm}\) | \(\lambda_{em} / \text{nm}\) | \(\Phi_F\) | \(\tau_F / \text{ps}\) |
|-------------|----------------|-----------------------------|-----------------------------|----------|-----------------|
|             | \textbf{Pnc$_2$COOH} | –                          | 660                         | 0.016\(^{(b)}\) | <200\(^{(b,c)}\) |
| Toluene     | \textbf{SubPzOH}          | 562                         | –                           | 0.018     | 785             |
|             | \textbf{SubPzPnc$_2$}      | 562.5                       | 662                         | 0.019\(^{(d)}\) | <200\(^{(c,d)}\) |
|             | \textbf{Pnc$_2$COOH}       | –                          | 663                         | 0.016\(^{(b)}\) | <200\(^{(b,c)}\) |
| Anisole     | \textbf{SubPzOH}          | 561.5                       | –                           | 0.0051    | 683             |
|             | \textbf{SubPzPnc$_2$}      | 563                         | 664                         | 0.0059\(^{(d)}\) | <200\(^{(c,d)}\) |
| Benzonitrile| \textbf{Pnc$_2$COOH}       | –                          | 665.5                       | 0.016\(^{(b)}\) | <200\(^{(b,c)}\) |
|             | \textbf{SubPzOH}          | 560.5                       | –                           | 0.0020    | 598             |
|             | \textbf{SubPzPnc$_2$}      | 562.5                       | 666.5                       | 0.003\(^{(d)}\) | <200\(^{(c,d)}\) |

\(^{(a)}\) Values refer to the SubPz centered fluorescence if not stated otherwise. \(^{(b)}\) Values refer to the Pnc$_2$ centered fluorescence. \(^{(c)}\) Lifetime is below the resolution limit of our time-correlated single photon counting (TCSPC) setup. \(^{(d)}\) SubPz centered fluorescence is not detectable / under the Pnc$_2$ centered emission in the conjugate.
Figure S27. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{\text{ex}} = 633$ nm) of Pnc$_2$COOH in xylene with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 453, 508, 608, and 658 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of Pnc$_2$COOH shown in a), with the initially formed Pnc$_2$COOH singlet excited state $^1(S_1S_0)_{\text{Pnc}_2\text{COOH}}$ (red), intermediate state $^1CT(S_1S_0)_{\text{Pnc}_2\text{COOH}}$ (blue), and correlated triplet pair state $^1(T_1T_1)_{\text{Pnc}_2\text{COOH}}$ (green); inset displays the relative populations of the respective SASs.
Figure S28. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{ex} = 480$ nm) of SubPzOH in toluene with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 430, 562, 630, and 1052 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of SubPzOH shown in (a), with the initially formed singlet excited state $^1(S_1)_{SubPzOH}$ (black) and triplet excited state $^3(T_1)_{SubPzOH}$ (orange); inset displays the relative populations of the respective SASs. (c) Differential absorption spectra obtained from nsTA measurements ($\lambda_{ex} = 480$ nm) of SubPzOH in toluene with several time delays between 0 and 400 $\mu$s (colored solid lines) at rt; inset displays kinetics at 430, 562, 630, and 1000 nm (colored dots). (d) Species associated spectra (SAS) of the nsTA data of SubPzOH shown in (c), with the initially formed singlet excited state $^1(S_1)_{SubPzOH}$ (black) and triplet excited state $^3(T_1)_{SubPzOH}$ (orange); inset displays the relative populations of the respective SASs.
Figure S29. (a) Differential absorption spectra obtained from fsTA measurements (λ_{ex} = 633 nm) of Pnc₂COOH in toluene with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 451, 506, 606, and 663 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of Pnc₂COOH shown in a), with the initially formed Pnc₂COOH singlet excited state \(^1(S_1-S_0)_{Pnc2COOH}\) (red), intermediate state \(^{CT}(S_1-S_0)_{Pnc2COOH}\) (blue), and correlated triplet pair state \(^1(T_1-T_1)_{Pnc2COOH}\) (green); inset displays the relative populations of the respective SASs.
Figure S30. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{\text{ex}} = 480$ nm) of $\text{SubPzPnc}_2$ in toluene with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 450, 506, 562, and 660 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of $\text{SubPzPnc}_2$ shown in (a), with the initially formed SubPz singlet excited state $^1(S_1)^{\text{SubPz}, \text{SubPzPnc}_2}$ (black), the Pnc$_2$ singlet excited state $^1(S_1S_0)^{\text{Pnc}_2, \text{SubPzPnc}_2}$ (red), intermediate state $^1(S_1S_0)^{\text{CT,Pnc}_2, \text{SubPzPnc}_2}$ (blue), and correlated triplet pair state $^1(T_1T_1)^{\text{Pnc}_2, \text{SubPzPnc}_2}$ (green); inset displays the relative populations of the respective SASs.
| Compound       | $t^1(S_1)_{SubPz}$ | $t^1(S_1S_0)_{Pnc2}$ | $t^1(T_1T_1)_{Pnc2}$ | TQY $^{a,b}$ | $t^1(S_1)_{SubPz}$ | $t^1(T_1)_{SubPz}$ |
|---------------|--------------------|---------------------|---------------------|--------------|--------------------|---------------------|
| SubPzOH       | 955 ps             | -                   | -                   | -            | 975 ps             | 80.06 µs            |
| Pnc2 COOH     | -                  | 8.86 ps             | 78.57 ps            | 3.25 ns      | 3.25 ns            | -                   |
| SubPzPnc2     | 3.37 ps            | 26.55 ps            | 115.01 ps           | 2.88 ns      | 152%               | n.r.$^c$            |

$^a$ Determined via following the intensification of the transient bleaching of the Pnc2 moiety and comparing the relative intensification of the species-associated for the $t^1(S_1S_0)_{Pnc2}$ and the $t^1(T_1T_1)_{Pnc2}$ state, respectively. $^b$ An error margin in the range of ±10% may be considered when determining the TQYs. $^c$n.r. = not resolvable. Lifetimes are either too long to be resolved with fsTA or too short to be resolved with nsTA.
Figure S31. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{ex} = 633$ nm) of Pnc$_2$COOH in anisole with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 453, 508, 608, and 658 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of Pnc$_2$COOH shown in a), with the initially formed Pnc$_2$COOH singlet excited state $1(S_1S_0)_{Pnc2COOH}$ (red), intermediate state $CT(S_1S_0)_{Pnc2COOH}$ (blue), and correlated triplet pair state $1(T_1T_1)_{Pnc2COOH}$ (green); inset displays the relative populations of the respective SASs.
Figure S32. (a) Differential absorption spectra obtained from fsTA measurements (λ_{ex} = 480 nm) of SubPzOH in anisole with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 430, 562, 630, and 1052 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of SubPzOH shown in (a), with the initially formed singlet excited state \( ^1(S_1)_{\text{SubPzOH}} \) (black) and triplet excited state \( ^3(T_1)_{\text{SubPzOH}} \) (orange); inset displays the relative populations of the respective SASs. (c) Differential absorption spectra obtained from nsTA measurements (λ_{ex} = 480 nm) of SubPzOH in anisole with several time delays between 0 and 400 μs (colored solid lines) at rt; inset displays kinetics at 450, 560, 630, and 1000 nm (colored dots). (d) Species associated spectra (SAS) of the nsTA data of SubPzOH shown in (c), with the initially formed singlet excited state \( ^1(S_1)_{\text{SubPzOH}} \) (black) and triplet excited state \( ^3(T_1)_{\text{SubPzOH}} \) (orange); inset displays the relative populations of the respective SASs.
Figure S33. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{ex} = 480$ nm) of SubPzPnc$_2$ in anisole with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 451, 507, 562, and 663 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of SubPzPnc$_2$ shown in (a), with the initially formed SubPz singlet excited state $1^1(S_1)_{SubPz,SubPzPnc2}$ (black), the Pnc$_2$ singlet excited state $1^1(S_1S_0)_{Pnc2,SubPzPnc2}$ (red), intermediate state CT$1^1(S_1S_0)_{Pnc2,SubPzPnc2}$ (blue), and correlated triplet pair state $1^1(T_1T_1)_{Pnc2,SubPzPnc2}$ (green); inset displays the relative populations of the respective SASs.
Table S3. Kinetic data from fsTA and nsTA measurements and triplet quantum yields (TQYs) for SubPzOH, Pnc$_2$COOH, and SubPzPnc$_2$ in anisole.

| Compound    | $\tau$(S$_1$)$_{SubPz}$ | $\tau$(S$_1$)$_{Pnc2}$ | $\tau$(T$_1$)$_{Pnc2}$ | TQY$^{a,b}$ | $\tau$(S$_1$)$_{SubPz}$ | $\tau$(T$_1$)$_{SubPz}$ |
|-------------|--------------------------|------------------------|------------------------|-------------|--------------------------|------------------------|
| SubPzOH     | 630 ps                   | -                      | -                      | -           | 719 ps                   | 180.00 µs              |
| Pnc$_2$COOH | -                       | 10.89 ps               | 105.54 ps              | 3.03 ns     | 137%                     | -                      |
| SubPzPnc$_2$| 5.57 ps                  | 25.94 ps               | 102.21 ps              | 2.30 ns     | 151%                     | n.r.$^c$               |

$^a$Determined via following the intensification of the transient bleaching of the Pnc$_2$ moiety and comparing the relative intensification of the species-associated for the $^1$(S$_1$S$_0$)$_{Pnc2}$ and the $^1$(T$_1$T$_1$)$_{Pnc2}$ state, respectively. $^b$An error margin in the range of ±10% may be considered when determining the TQYs. $^c$n.r. = not resolvable. Lifetimes are either too long to be resolved with fsTA or too short to be resolved with nsTA.
Figure S34. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{\text{ex}} = 480$ nm) of SubPzOH in benzonitrile with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 430, 562, 630, and 1052 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of SubPzOH shown in (a), with the initially formed singlet excited state $^{1}(S_{1})_{\text{SubPzOH}}$ (black) and triplet excited state $^{3}(T_{1})_{\text{SubPzOH}}$ (orange); inset displays the relative populations of the respective SASs. (c) Differential absorption spectra obtained from nsTA measurements ($\lambda_{\text{ex}} = 480$ nm) of SubPzOH in benzonitrile with several time delays between 0 and 400 $\mu$s (colored solid lines) at rt; inset displays kinetics at 455, 560, 617, and 1010 nm (colored dots). (d) Species associated spectra (SAS) of the nsTA data of SubPzOH shown in (c), with the initially formed singlet excited state $^{1}(S_{1})_{\text{SubPzOH}}$ (black) and triplet excited state $^{3}(T_{1})_{\text{SubPzOH}}$ (orange); inset displays the relative populations of the respective SASs.
Figure S35. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{ex} = 633$ nm) of Pnc$_2$COOH in benzonitrile with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 456, 513, 616, and 666 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of Pnc$_2$COOH shown in a), with the initially formed Pnc$_2$COOH singlet excited state $^1$(S$_1$S$_0$)Pnc$_2$COOH (red), intermediate state $^{CT}$(S$_1$S$_0$)Pnc$_2$COOH (blue), and correlated triplet pair state $^1$(T$_1$T$_1$)Pnc$_2$COOH (green); inset displays the relative populations of the respective SASs.
Figure S36. (a) Differential absorption spectra obtained from fsTA measurements ($\lambda_{\text{ex}} = 480$ nm) of SubPzPnc$_2$ in benzonitrile with several time delays between 0 and 5250 ps (colored solid lines) at rt; inset displays kinetics at 455, 510, 562, 665 nm (colored dots). (b) Species associated spectra (SAS) of the fsTA data of SubPzPnc$_2$ shown in (a), with the initially formed SubPz singlet excited state $^1$S$_{1}\text{SubPz}$,SubPzPnc$_2$ (black), the Pnc$_2$ singlet excited state $^1$(S$_1$S$_0$)$_{\text{Pnc2,SubPzPnc2}}$ (red), intermediate state $^1$(S$_1$S$_0$)$_{\text{Pnc2,SubPzPnc2}}$ (blue), and correlated triplet pair state $^1$(T$_1$T$_1$)$_{\text{Pnc2,SubPzPnc2}}$ (green); inset displays the relative populations of the respective SASs.
Table S4. Kinetic data from fsTA and nsTA measurements and triplet quantum yields (TQYs) for SubPzOH, Pnc₂COOH, and SubPzPnc₂ in benzonitrile.

| Compound       | t[S₁]SubPz | t[S₁S₀]Pnc₂ | t[C₁(S₁S₀)Pnc₂] | t[T₁T₁]Pnc₂ | TQY¹,²   | nsTA      | t[S₁]SubPz | t[T₁]SubPz |
|----------------|------------|-------------|-----------------|-------------|---------|-----------|------------|------------|
| SubPzOH        | 532.02 ps  | -           | -               | -           | -       | 632.00 ps | 111.30 μs  |
| Pnc₂COOH       | -          | 14.52 ps    | 116.03 ps       | 3.24 ns     | 142%    | -         | -          |
| SubPzPnc₂      | 8.65 ps    | 24.44 ps    | 116.09 ps       | 2.44 ns     | 161%    | n.r.      | -          |

¹Determined via following the intensification of the transient bleaching of the Pnc₂ moiety and comparing the relative intensification of the species-associated for the C₁(S₁S₀)Pnc₂ and the ¹(T₁T₁)Pnc₂ state, respectively. ²An error margin in the range of ±10% may be considered when determining the TQYs. ³n.r. = not resolvable. Lifetimes are either too long to be resolved with fsTA or too short to be resolved with nsTA.
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