

Electronic supplementary information

Bridge control of photophysical properties in benzothiazole-phenoxazine emitters – from thermally activated delayed fluorescence to room temperature phosphorescence

Simon Paredis,^{a,b} Tom Cardeynaels,^{a,b,c} Jasper Deckers,^{a,b} Andrew Danos,^d Dirk Vanderzande,^{a,b} Andrew P. Monkman,^d Benoît Champagne^c and Wouter Maes^{*,a,b}

^a Hasselt University, Institute for Materials Research (IMO-IMOMECE), Design & Synthesis of Organic Semiconductors (DSOS), Agoralaan 1, 3590 Diepenbeek, Belgium; E-mail: wouter.maes@uhasselt.be

^b IMOMECE Division, IMEC, Wetenschapspark 1, 3590 Diepenbeek, Belgium

^c University of Namur, Laboratory of Theoretical Chemistry, Theoretical and Structural Physical Chemistry Unit, Namur Institute of Structured Matter, Rue de Bruxelles 61, 5000 Namur, Belgium

^d OEM group, Department of Physics, Durham University, South Road, Durham DH1 3LE, United Kingdom

Table of contents

1. Materials and methods	S2
2. Materials synthesis	S3
3. Ground – excited state electron density differences	S5
4. Additional TD(DFT) data	S6
5. Simulated UV-Vis absorption spectra	S7
6. Absorption and emission spectra and data in different solvents	S8
7. Relaxed potential energy surface scans	S3
8. Photodegradation	S3
9. Time-resolved emission spectra in zeonex	S3
10. Steady-state emission spectra in air and under inert atmosphere in zeonex film	S3
11. Laser energy experiments	S3
12. Time-resolved emission spectra in solution	S3
13. Singlet oxygen generation	S3
14. NMR spectra	S3
15. Coordinates of optimized geometries	S37

1. Materials and methods

All reagents and chemicals were obtained from commercial sources and used without further purification. Dry solvents were obtained from an MBraun solvent purification system (MB SPS-800) equipped with alumina columns. Preparative (recycling) size exclusion chromatography (SEC) was performed on a JAI LC-9110 NEXT system equipped with JAIGEL 1H and 2H columns (eluent chloroform, flow rate 3.5 mL min⁻¹). Proton and carbon nuclear magnetic resonance (¹H and ¹³C NMR) spectra were obtained on a Varian or Jeol spectrometer operating at 400 MHz for ¹H (100 MHz for ¹³C). Chemical shifts (δ) are given in ppm relative to CDCl₃ ($\delta = 7.26$ ppm for ¹H NMR, $\delta = 77.06$ ppm for ¹³C NMR). Electrospray ionisation - mass spectrometry (ESI-MS) was performed using an LTQ Orbitrap Velos Pro mass spectrometer (ThermoFisher Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the m/z range 220–2000 using a standard solution containing caffeine, MRFA, and Ultramark 1621. A constant spray voltage of 5 kV was used and a nitrogen flow was applied at a dimensionless sheath gas flow rate of 7. The capillary temperature was set to 275 °C. A solvent mixture of HPLC grade THF and methanol (3:2) was used. Spectra were analysed via Thermo Xcalibur Qual Browser software.

Electronic absorption spectra of the small molecule chromophores in solution were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer from Agilent Technologies. Corrected steady-state excitation and emission spectra of the chromophore solutions were recorded on a Horiba-Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a 450 W Xe lamp as the light source, with an excitation wavelength (λ_{exc}) depending on the fluorescence quantum yield standard used and a slit width of 2 nm. Freshly prepared samples in 1 cm quartz cells were used to perform all UV-Vis-NIR absorption and fluorescence measurements. The fluorescence measurements were done under a right-angle arrangement. The standard uncertainty (square root of the variance) on the absorption and emission maxima is approximately 1 nm. Spectroscopic measurements under normal atmosphere were done in non-degassed spectroscopic grade solvents at 20 °C. Inert atmosphere was created by three consecutive freeze-pump-thaw cycles.

For the determination of the relative fluorescence quantum yields (Φ_f) in toluene, dilute solutions with an absorbance around 0.1 at the excitation wavelength were used. Quinine ($\lambda_{exc} = 347$ nm, $\Phi_f = 0.58$ in 0.1 M H₂SO₄ solution) was used as a standard to determine the fluorescence quantum yields.¹ The fluorescence quantum yield of the tested compound (Φ_x) was calculated using Equation (1), in which Φ_{st} is the fluorescence quantum yield of the standard, F_x and F_{st} are the integrated fluorescence of the test compound and the standard, A_x and A_{st} are the absorbance of the test compound and the standard at the excitation wavelength, and n_x and n_{st} are the refractive indices of the solvents in which the test compound and the standard were dissolved, respectively.

$$\Phi_x = \Phi_{st} \frac{F_x(1-10^{-A_{st}})n_x^2}{F_{st}(1-10^{-A_x})n_{st}^2} \quad (1)$$

1,3-Diphenylisobenzofuran (1,3-DPBF) was used as a singlet oxygen (¹O₂) scavenger to determine the singlet oxygen quantum yields (Φ_Δ). The ¹O₂ production was monitored by following the absorbance of 1,3-DPBF at 414 nm upon excitation of the respective chromophore at 325 nm using a single LED325W2 from Thorlabs ($\lambda_{exc} = 325 \pm 5$ nm, fwhm = 11 nm, $P = 1.7$ mW). To determine Φ_Δ , a relative method was used according to Equation (2). Here, x and st represent the sample and the standard, while Φ , A , m , and n represent the singlet oxygen quantum yield, the absorbance at the excitation wavelength ($\lambda_{exc} = 325$ nm), the slope of the decrease in absorbance of 1,3-DPBF over time, and the refractive index of the solvent used for the measurement, respectively. Optically matched solutions with an absorbance around 0.6 at 414 nm and 0.3 at 325 nm were used. Coronene was used as the standard ($\Phi_\Delta = 0.90$ in spectrograde toluene).² The solutions were continuously stirred during all measurements using a Cimareci magnetic stirrer.

1. A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.

2. F. Wilkinson, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113–262.

$$\Phi_x = \Phi_{st} \left(\frac{1-10^{-A_{st}}}{1-10^{-Ax}} \right) \left(\frac{m_x}{m_{st}} \right) \left(\frac{n_x}{n_{st}} \right)^2 \quad (2)$$

Molar extinction coefficients were obtained by dissolving ca. 1 mg of the respective benzothiazole-phenoxazine molecule in toluene (ca. 2 mL). This stock solution was serially diluted to yield different dye concentrations from which absorption spectra were obtained in quartz cells with 1 cm optical path length (l). Minimal three solutions with an absorbance between 0.01 and 0.1 at $\lambda_{obs}(max)$ were used to plot the absorbance (A) versus molar concentration (c). The molar extinction coefficient (ϵ) was then determined using the Beer-Lambert law as given in Equation (3).

$$A = \epsilon lc \quad (3)$$

Zeonex films were prepared via drop-casting using a mixture of the emitter and host (zeonex) in toluene at 1 wt%. The initial solution concentrations were 100 mg mL⁻¹ of zeonex and 1 mg mL⁻¹ of emissive material, combined in equal volumes. The films were drop-casted onto a quartz substrate at 65 °C to facilitate evaporation of the solvent. Absorption and emission spectra of the films were collected using a UV-3600 double beam spectrophotometer (Shimadzu) and a Fluoromax fluorimeter (Jobin Yvon). Time-resolved photoluminescence spectra and decays were recorded using a nanosecond gated spectrograph-coupled iCCD (Stanford) using an Nd:YAG laser emitting at 355 nm (EKSPLA) under vacuum for films or following freeze-pump-thaw cycles or argon bubbling for solutions. Laser power experiments were conducted using an N₂ laser (Lasertechnik Berlin) emitting at 337 nm with the same nanosecond gated spectrograph-coupled iCCD (Stanford) camera, attenuating the excitation using reflective neutral density filters. Photodegradation experiments were performed before and after intermittent periods of light irradiation with a 325 nm LED (1.7 mW). The solution was purged with nitrogen to minimise the amount of oxygen in the samples. Photoluminescence quantum yields in film were determined using a calibrated integrating sphere (Horiba Quanta-Phi) fibre-coupled to a spectrofluorometer (Horiba Fluorolog) as excitation source (400 nm) and as detection system. For the measurements in inert atmosphere, the sphere was flushed with a stream of dry nitrogen for at least 30 min to prevent oxygen quenching of triplets.

2. Materials synthesis

2-(4-bromophenyl)benzo[d]thiazole (**BTaz-Ph**)

General procedure 1: 4-Bromobenzaldehyde (169.2 mg, 914.5 μ mol), 2-aminobenzenethiol (119.5 mg, 954.5 μ mol), and sodium metabisulfite (186.9 mg, 983.2 μ mol) were dissolved in DMF (5 mL) and the mixture was stirred under reflux for 2 h. Afterwards, the reaction mixture was cooled down to room temperature, water was added, and an extraction with ethyl acetate was performed. The combined organic phase was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica) with CH₂Cl₂/petroleum ether (v/v = 40/60) as the eluent. 2-(4-Bromophenyl)benzo[d]thiazole was obtained as a yellow solid in 65% yield (172.4 mg). ¹H NMR (400 MHz, CDCl₃): 8.07 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.51 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.40 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 166.8, 154.2, 135.1, 132.6, 132.3, 129.0, 126.6, 125.6, 125.5, 123.4, 121.8. MS (ESI+) Calcd. for C₁₃H₉BrNS [M+H]⁺: m/z 289.9639 (100%), found: 289.9624.

2-(6-bromonaphthalen-2-yl)benzo[d]thiazole (**BTaz-Na**)

Synthesis according to general procedure 1: 6-bromo-2-naphthaldehyde (201.4 mg, 856.7 μ mol), 2-aminobenzenethiol (114.0 mg, 910.6 μ mol), sodium metabisulfite (167.5 mg, 881.1 μ mol), DMF (5 mL), eluent CH₂Cl₂/petroleum ether (v/v = 60/40); 64% yield (185.2 mg). ¹H NMR (400 MHz, CDCl₃): 8.53 (s, 1H), 8.22 (dd, J = 8.6, 1.8 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.62 (dd, J = 8.7, 2.0 Hz, 1H), 7.52 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.42 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 167.7, 154.3, 135.6, 135.2, 131.7, 131.52,

130.51, 130.50, 130.1, 128.0, 127.5, 126.7, 125.7, 125.6, 123.5, 121.84, 121.80. MS (ESI+) Calcd. for C₁₇H₁₁BrNS [M+H]⁺: *m/z* 339.9796 (100%), found: 339.9760.

2-(5-bromothiophen-2-yl)benzo[d]thiazole (**BTaz-Th**)

Synthesis according to general procedure 1: 5-bromothiophene-2-carbaldehyde (280 μL, 2.35 mmol), 2-aminobenzenethiol (289.2 mg, 2.31 mmol), sodium metabisulfite (448 mg, 2.36 mmol), DMF (10 mL), eluent CH₂Cl₂/petroleum ether (v/v = 40/60); 17% yield (118.3 mg). ¹H NMR (400 MHz, CDCl₃): 8.01 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.39 (d, *J* = 4.0 Hz, 1H), 7.38 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.08 (d, *J* = 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 160.4, 153.6, 138.9, 134.6, 131.1, 128.6, 126.7, 125.6, 123.2, 121.7, 117.3. MS (ESI+) Calcd. for C₁₁H₇BrNS₂ [M+H]⁺: *m/z* 295.9203 (100%), found: 295.9186.

10-(4-(benzo[d]thiazol-2-yl)phenyl)-10H-phenoxazine (**BTaz-Ph-PXZ**)

General procedure 2: 2-(4-Bromophenyl)benzo[d]thiazole (153.0 mg, 527 μmol), 10H-phenoxazine (109.1 mg, 595.5 μmol), palladium(II) acetate (11.8 mg, 52.7 μmol), tri-*tert*-butylphosphine (21.2 mg, 105.0 μmol), and sodium *tert*-butoxide (111.3 mg, 1.16 mmol) were dissolved in dry toluene (12 mL) under argon atmosphere. The mixture was heated to reflux for 16 h while stirring and then cooled down to room temperature and concentrated under reduced pressure. The crude product was purified by column chromatography (silica) with CH₂Cl₂/petroleum ether (v/v = 50/50) as the eluent. **BTaz-Ph-PXZ** was further purified using preparative (recycling) SEC and was obtained as a yellow solid (115.8 mg, 58%). ¹H NMR (400 MHz, CDCl₃): 8.32 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.56–7.48 (m, 3H), 7.44 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 6.82–6.42 (m, 6H), 6.02 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): 166.8, 154.3, 144.1, 141.6, 135.4, 134.1, 133.8, 131.7, 130.3, 126.7, 125.7, 123.6, 123.5, 121.9, 121.8, 115.8, 113.4. MS (ESI+) Calcd. for C₂₅H₁₇N₂O₅ [M+H]⁺: *m/z* 393.1061, found: 393.1027.

10-(6-(benzo[d]thiazol-2-yl)naphthalen-2-yl)-10H-phenoxazine (**BTaz-Na-PXZ**)

Synthesis according to general procedure 2: 2-(6-bromonaphthalen-2-yl)benzo[d]thiazole (157.0 mg, 461 μmol), 10H-phenoxazine (93.3 mg, 508 μmol), palladium(II) acetate (10.4 mg, 46.1 μmol), tri-*tert*-butylphosphine (18.7 mg, 92.3 μmol), sodium *tert*-butoxide (88.7 mg, 88.7 μmol), dry toluene (12 mL), eluent CH₂Cl₂/petroleum ether (v/v = 50/50); yellow solid (138.7 mg, 68%). ¹H NMR (400 MHz, CDCl₃): 8.66 (s, 1H), 8.29 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.15 (ddd, *J* = 8.2, 1.3, 0.7 Hz, 1H), 8.01–7.94 (m, 2H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.55 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.50 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.44 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.73 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.67 (td, *J* = 7.6, 1.5 Hz, 2H), 6.59 (td, *J* = 7.7, 1.7 Hz, 2H), 5.99 (dd, *J* = 7.9, 1.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): 167.7, 154.4, 144.1, 137.9, 136.0, 135.3, 134.3, 132.9, 132.4, 132.2, 130.2, 129.3, 129.0, 127.5, 126.7, 125.7, 125.4, 123.5, 123.4, 121.9, 121.7, 115.7, 113.6. MS (ESI+) Calcd. for C₂₉H₁₈N₂O₅ [M+H]⁺: *m/z* 443.1218, found: 443.1203.

10-(5-(benzo[d]thiazol-2-yl)thiophen-2-yl)-10H-phenoxazine (**BTaz-Th-PXZ**)

Synthesis according to general procedure 2: 2-(5-bromothiophen-2-yl)benzo[d]thiazole (118 mg, 398 μmol), 10H-phenoxazine (79.2 mg, 432 μmol), palladium(II) acetate (8.9 mg, 40 μmol), tri-*tert*-butylphosphine (16.1 mg, 80 μmol), sodium *tert*-butoxide (76.6 mg, 797 μmol), dry toluene (12 mL), eluent CH₂Cl₂/petroleum ether (v/v = 40/60); yellow solid (115.8 mg, 75%). ¹H NMR (400 MHz, CDCl₃): 8.04 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.07 (d, *J* = 3.9 Hz, 1H), 6.78–6.70 (m, 6H), 6.40 (dt, *J* = 7.3, 1.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): 161.0, 153.7, 144.1, 137.5, 134.8, 133.6, 129.7, 127.9, 126.8, 125.7, 123.7, 123.4, 122.8, 121.7, 115.9, 114.4. MS (ESI+) Calcd. for C₂₃H₁₅N₂O₅ [M+H]⁺: *m/z* 399.0626, found: 399.0606.

3. Ground – excited state electron density differences

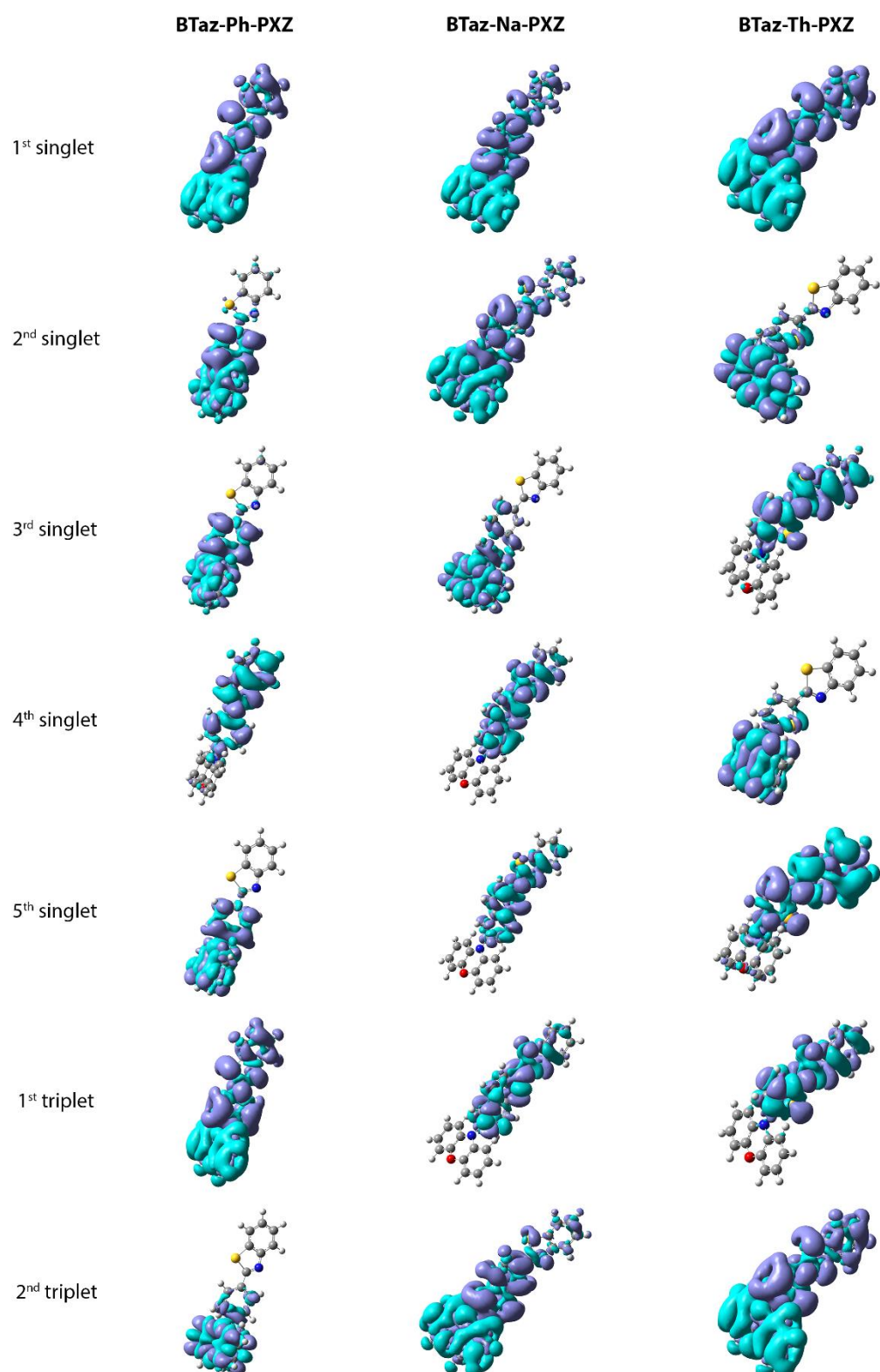


Figure S1: Ground – excited state electron density differences for the singlet and triplet excited states of **BTaz-Ph-PXZ** (left), **BTaz-Na-PXZ** (middle), and **BTaz-Th-PXZ** (right). Purple areas indicate increased electron density, while cyan areas point to decreased electron density (isosurface value = 0.0004 a.u. for all densities).

4. Additional TD(DFT) data

Table S1: TDDFT results for the third, fourth, and fifth vertical singlet excitation energies and the corresponding oscillator strengths (f) as determined with TDDFT-TDA and a modified LC-BLYP ($\omega = 0.17 \text{ bohr}^{-1}$) exchange correlation functional.

Compound	S_3 (eV)	f_{S_3}	S_4 (eV)	f_{S_4}	S_5 (eV)	f_{S_5}
BTaz-Ph-PXZ	3.86	0.101	4.15	0.806	4.26	0.136
BTaz-Na-PXZ	3.82	0.061	3.93	1.031	4.05	0.227
BTaz-Th-PXZ	3.90	1.043	4.18	0.194	4.27	0.110

Table S2: Nature of the various transitions ($H = \text{HOMO}$, $L = \text{LUMO}$), charge-transfer distance (d_{CT}), and change in dipole moment ($\Delta\mu$, excited state dipole – ground state dipole) accompanying the $S_0 \rightarrow S_x$ ($x = 3, 4, 5$) transitions in cyclohexane, as determined with TDDFT-TDA and a modified LC-BLYP ($\omega = 0.17 \text{ bohr}^{-1}$) exchange correlation functional.

Compound	S_3			S_4			S_5		
	Nature	d_{CT} (Å)	$\Delta\mu$ (D)	Nature	d_{CT} (Å)	$\Delta\mu$ (D)	Nature	d_{CT} (Å)	$\Delta\mu$ (D)
BTaz-Ph-PXZ	H→L+3	1.636	4.680	H-2→L	1.726	3.325	H→L+7	1.210	2.797
BTaz-Na-PXZ	H→L+2	1.140	3.047	H-1→L	0.980	1.771	H-3/4→L	0.744	1.019
BTaz-Th-PXZ	H-1→L	0.840	1.512	H→L+5	0.458	0.878	H-3→L	2.734	6.597

Table S3: Orbital energies for **BTaz-Ph-PXZ**, **BTaz-Na-PXZ**, and **BTaz-Th-PXZ** as obtained using DFT with LC-BLYP ($\omega = 0.17 \text{ bohr}^{-1}$)/6-311G(d).

	HOMO-1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)
BTaz-Ph-PXZ	-7.745	-6.258	-0.698	0.461
BTaz-Na-PXZ	-7.506	-6.275	-0.820	-0.057
BTaz-Th-PXZ	-7.559	-6.387	-0.779	0.758

5. Simulated UV-Vis absorption spectra

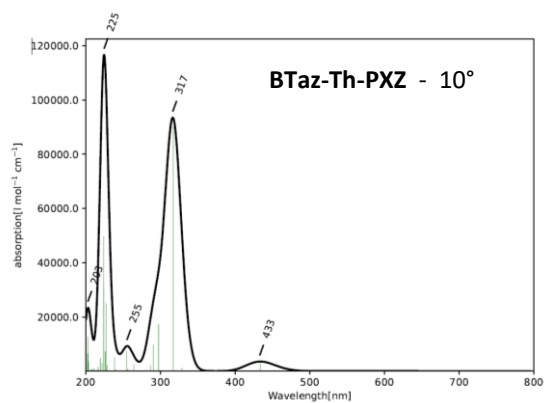
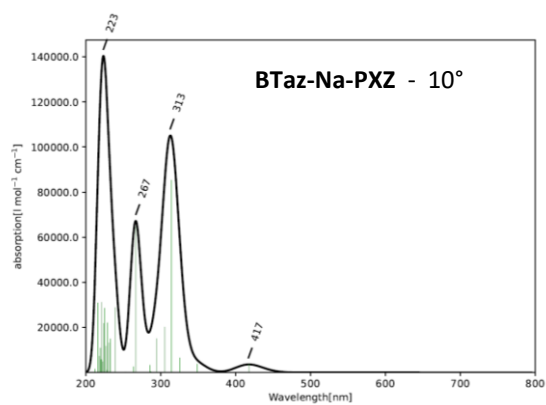
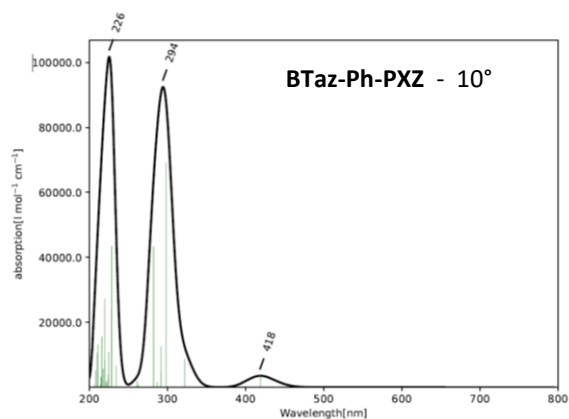


Figure S2: Simulated UV-Vis absorption spectra derived from the TDDFT results for the optimized geometries with a modified dihedral angle of $\pm 10^\circ$ to account for the vibrational freedom of the PXZ moiety with respect to the rest of the molecule. A full-width at half maximum of 0.3 eV was applied for every excitation energy.

6. Absorption and emission spectra and data in different solvents

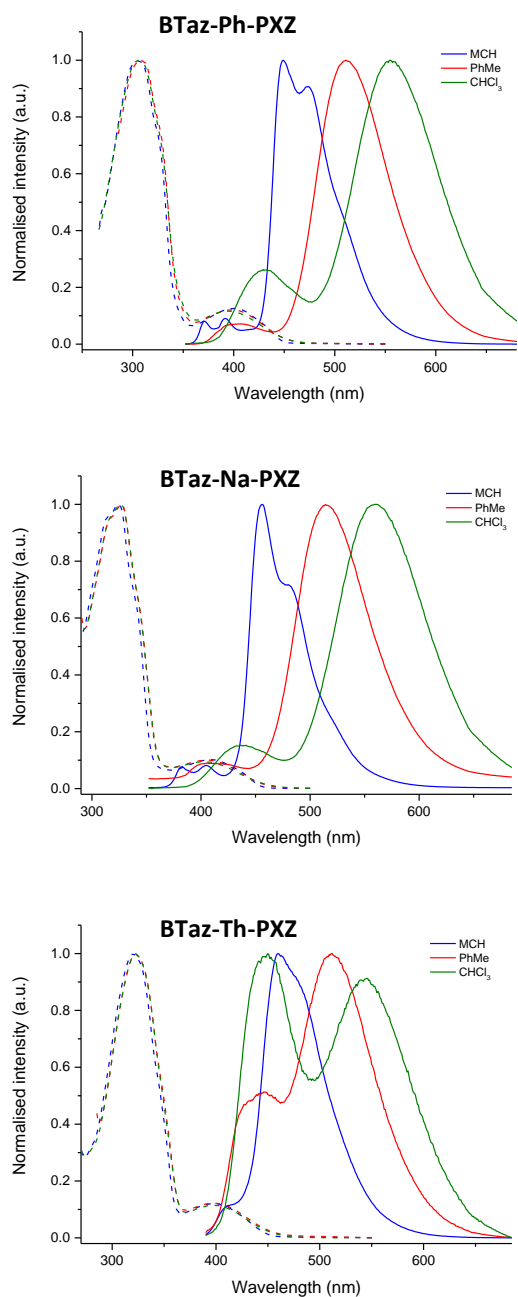


Figure S3: Normalised steady-state absorption (dotted lines) and emission (solid lines; $\lambda_{exc} = 340$ nm) spectra in methylcyclohexane (MCH), toluene (PhMe), and chloroform (CHCl₃) for **BTaz-Ph-PXZ** (top), **BTaz-Na-PXZ** (middle), and **BTaz-Th-PXZ** (bottom).

Table S4: Additional spectroscopic data for **BTaz-Ph-PXZ**, **BTaz-Na-PXZ**, and **BTaz-Th-PXZ**.

Compound	Solvent ^[a]	λ_{abs} (nm) ^[b]	λ_{em} (nm) ^[c]	Φ_f ^[d]
BTaz-Ph-PXZ	Methylcyclohexane	306, 401	391, 449	0.10
	Toluene	308, 401	407, 513	0.22
	Chloroform	306, 395	429, 555	0.12
BTaz-Na-PXZ	Methylcyclohexane	324, 410	405, 456	0.10
	Toluene	327, 405	406, 516	0.13
	Chloroform	327, 404	441, 559	0.13
BTaz-Th-PXZ	Methylcyclohexane	320, 398	411, 460	0.05
	Toluene	323, 397	446, 514	0.02
	Chloroform	323, 398	450, 546	0.02

^[a] Spectrograde solvents were used for all measurements. Solvents are listed from top to bottom according to increasing polarity $E_T(30)$. ^[b] Absorption maxima. ^[c] Fluorescence emission maxima. ^[d] Fluorescence quantum yields under normal atmosphere determined vs quinine ($\Phi_f = 0.58$, $\lambda_{exc} = 347$ nm) in 0.1 M H_2SO_4 solution as a reference.

7. Relaxed potential energy surface scans

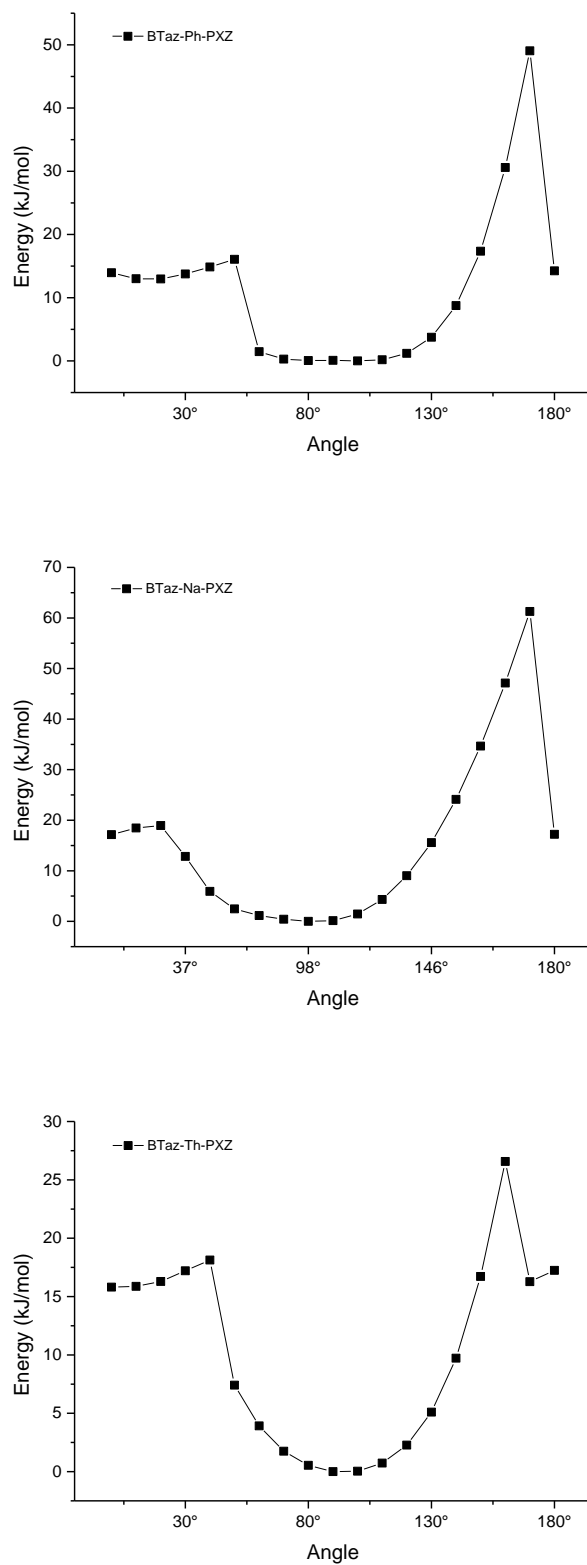


Figure S4: Relaxed potential energy surface scans for *BTaz-Ph-PXZ* (top), *BTaz-Na-PXZ* (middle), and *BTaz-Th-PXZ* (bottom). These calculations were performed using the M06/6-311G(d) method.³

8. Photodegradation



Figure S5: Photograph of a cuvette containing a *BTaz-Ph-PXZ* solution in chloroform after irradiation with an N_2 laser emitting at 337 nm, showing a clear colour change on the top part of the solution where the light hits the sample, whereas the bottom part retains the same colour as the pristine solution. This colour change was not, or barely, visible in toluene.

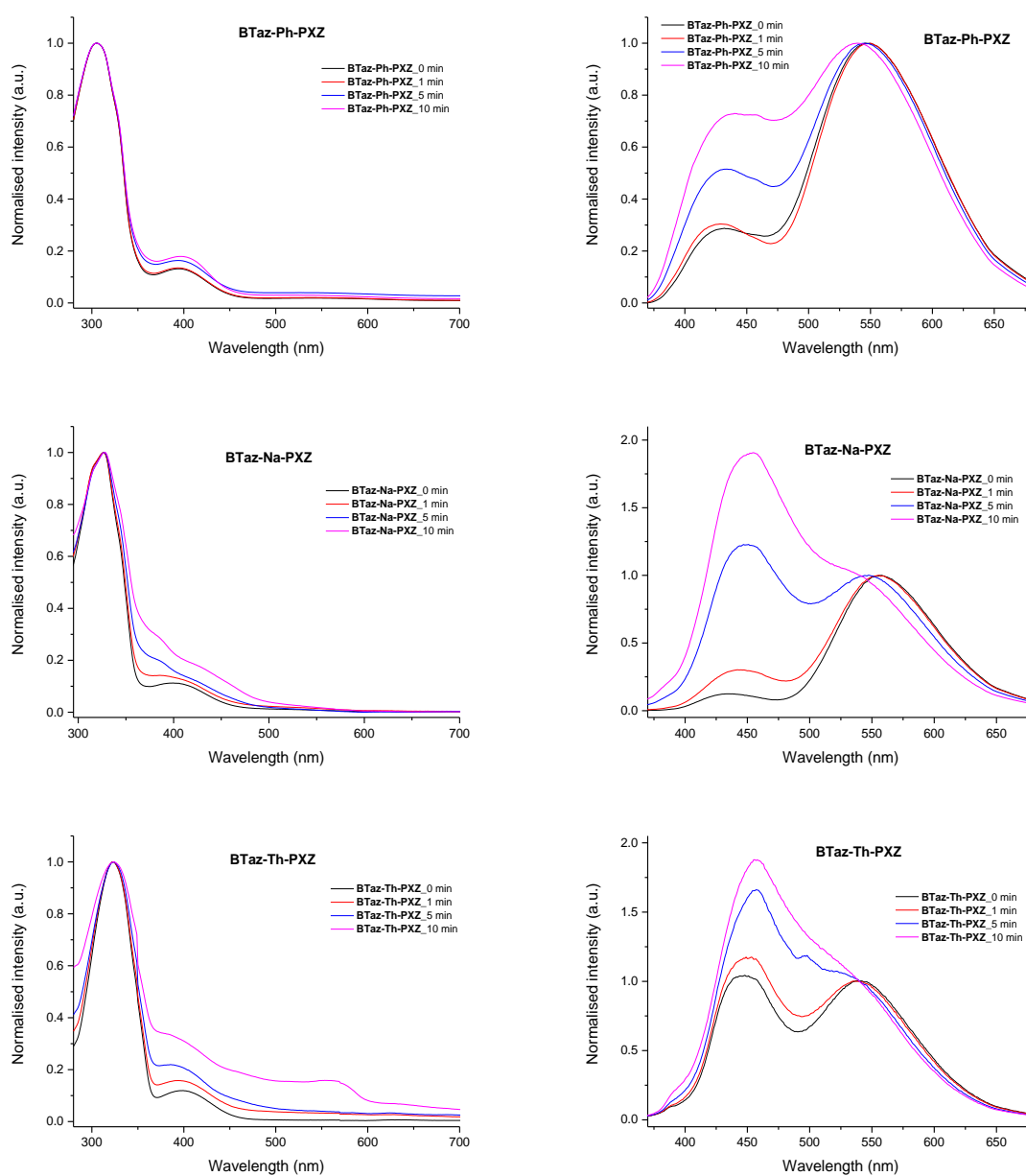


Figure S6: Absorption (left) and emission (right) spectra of *BTaz-Ph-PXZ* (top), *BTaz-Na-PXZ* (middle), and *BTaz-Th-PXZ* (bottom) in chloroform recorded after intermittent periods of irradiation with a 325 nm LED (1.7 mW).

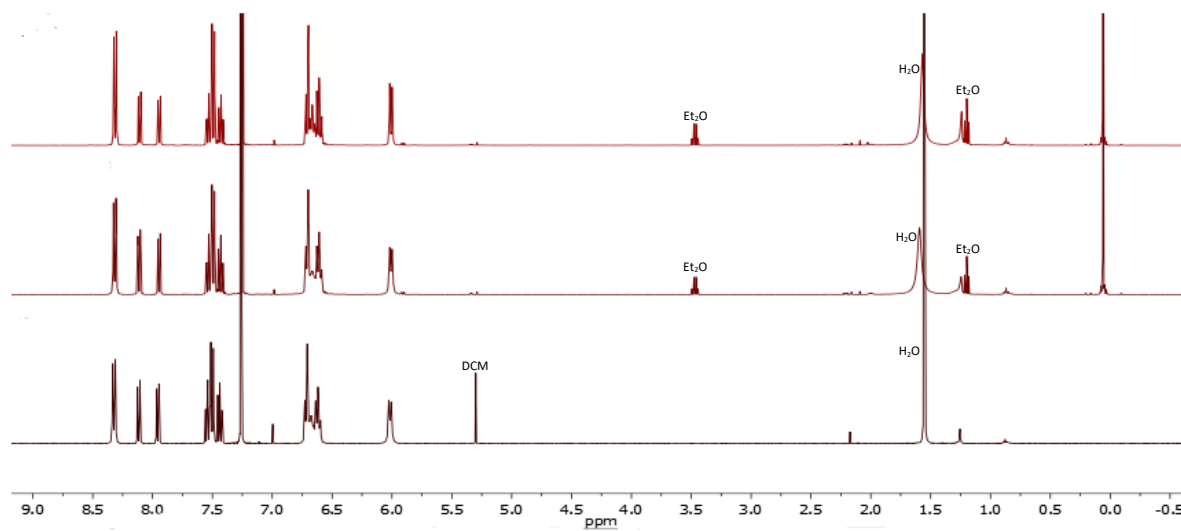


Figure S7: ^1H NMR spectra of **BTaz-Ph-PXZ** before irradiation (bottom) and after irradiating with a 325 nm LED (1.7 mW) for 30 min (middle) and 60 min (top).

9. Time-resolved emission spectra in zeonex

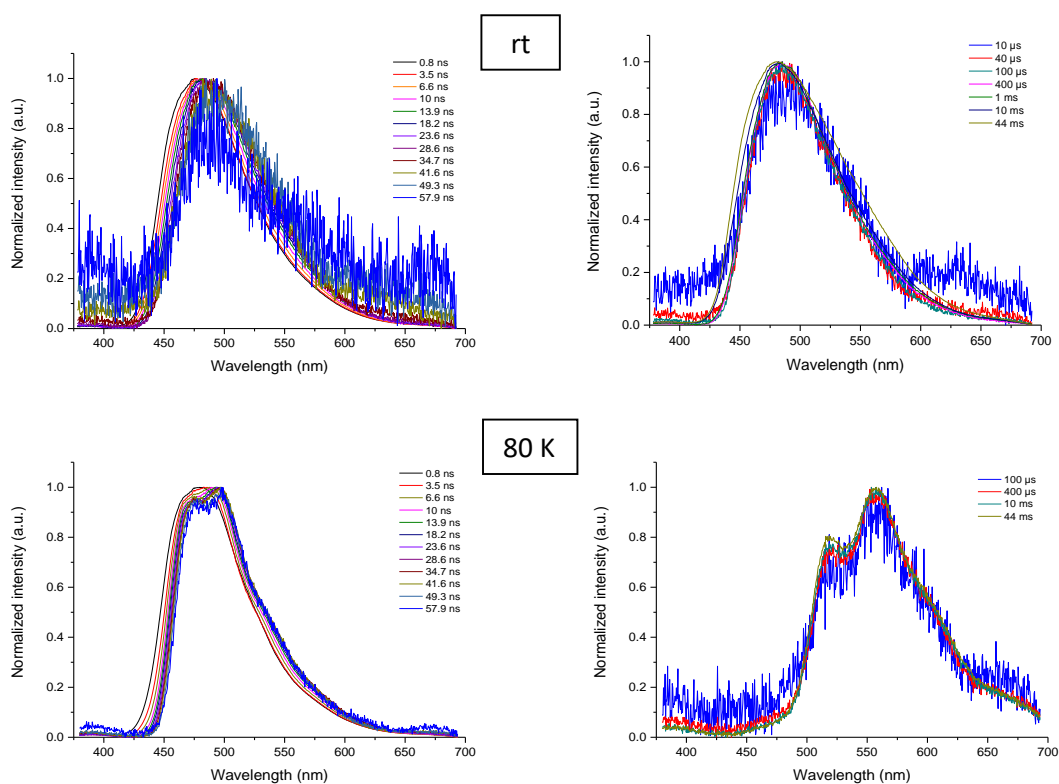


Figure S8: Snapshots of the emission at various time scales during prompt (left) and delayed emission (right) for **BTaz-Ph-PXZ** in zeonex at room temperature (top) and at 80 K (bottom).

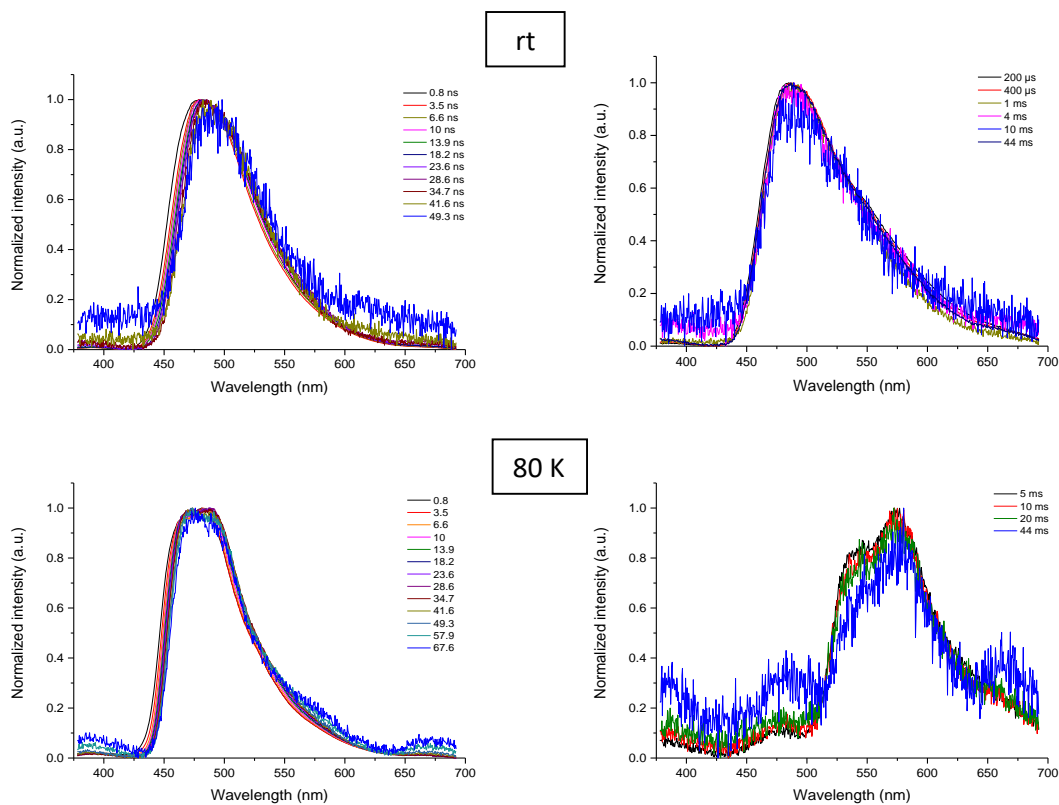


Figure S9: Snapshots of the emission at various time scales during prompt (left) and delayed emission (right) for **BTaz-Na-PXZ** in zeonex at room temperature (top) and at 80 K (bottom).

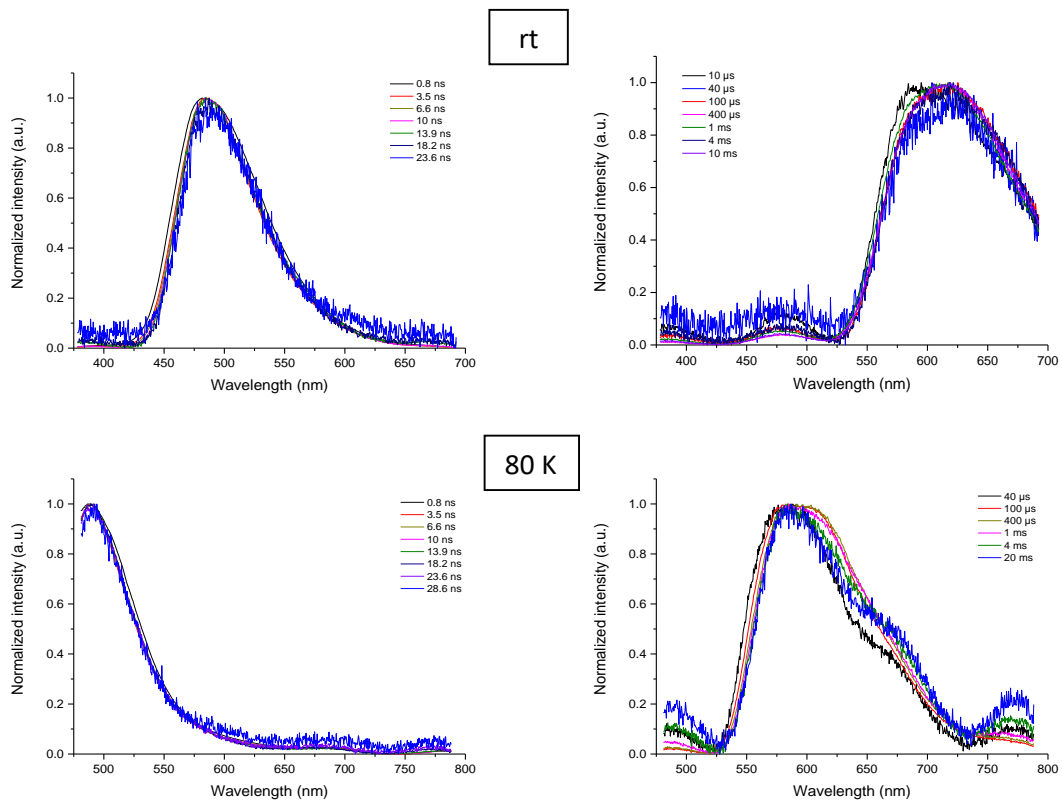


Figure S10: Snapshots of the emission at various time scales during prompt (left) and delayed emission (right) for **BTaz-Th-PXZ** in zeonex at room temperature (top) and at 80 K (bottom).

10. Steady-state emission spectra in air and under inert atmosphere in zeonex film

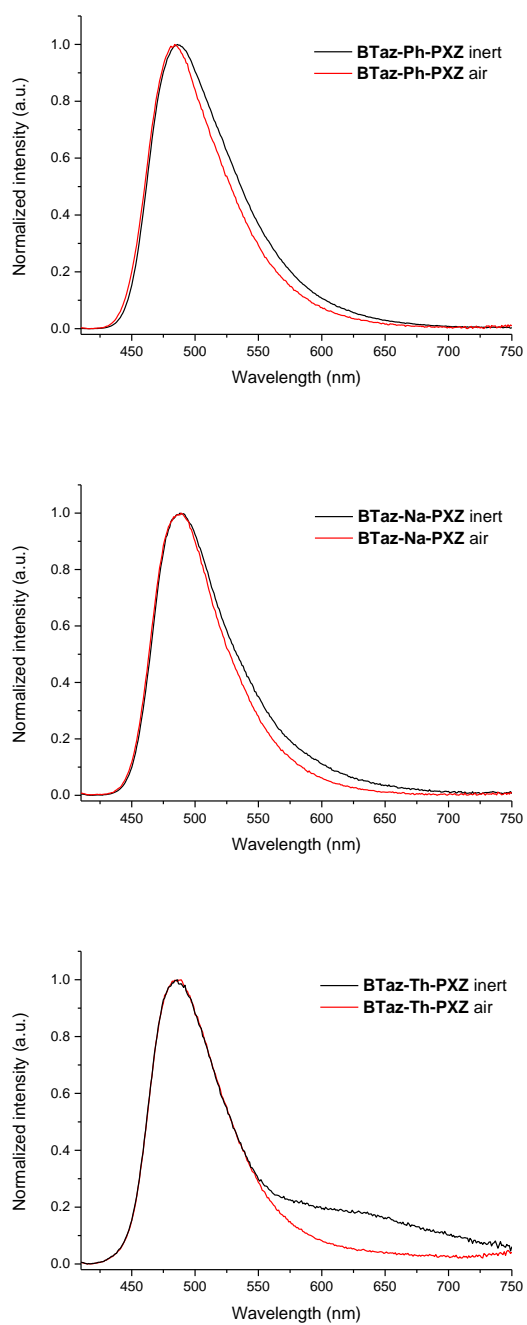


Figure S11: Normalised steady-state emission ($\lambda_{exc} = 400$ nm) spectra measured in inert atmosphere (black) and in air (red) in zeonex for **BTaz-Ph-PXZ** (top), **BTaz-Na-PXZ** (middle), and **BTaz-Th-PXZ** (bottom).

11. Laser energy experiments

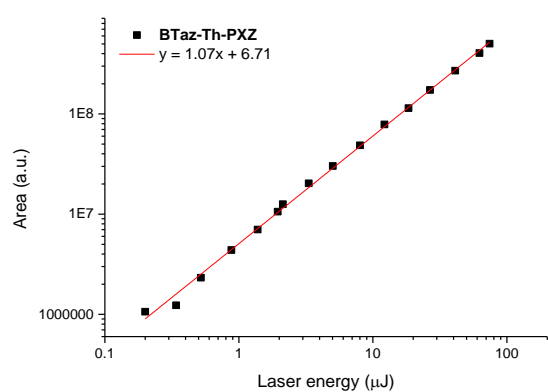
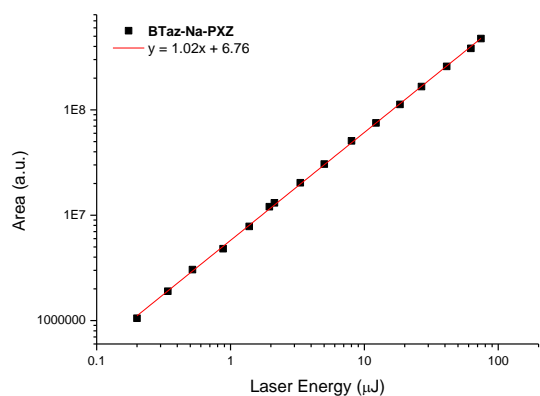
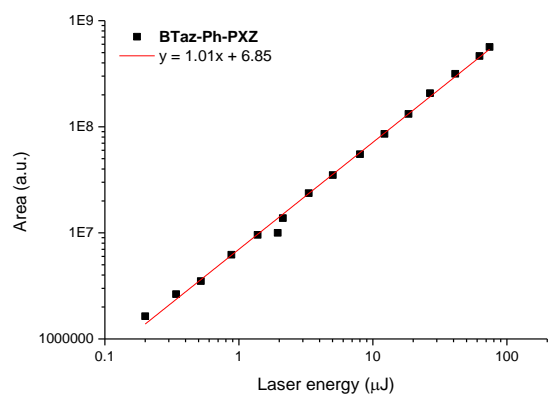


Figure S12: Laser power experiments using an N_2 laser for **BTaz-Ph-PXZ** (top; time delay = 50 μs , integration time = 50 μs to 250 μs), **BTaz-Na-PXZ** (middle; time delay = 150 μs , integration time = 150 μs to 2150 μs), and **BTaz-Th-PXZ** (bottom; time delay = 50 μs , integration time = 50 μs to 450 μs).

12. Time-resolved emission spectra in solution

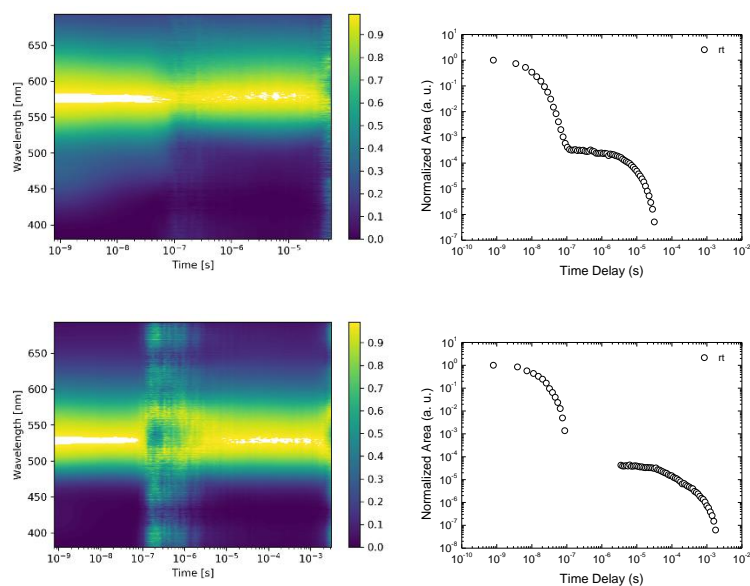


Figure S13: Normalised time-resolved emission spectra for **BTaz-Ph-PXZ** in chloroform (top) and toluene (bottom) at room temperature, with the decay of the total emission. Data points without signal have been omitted from the decay.

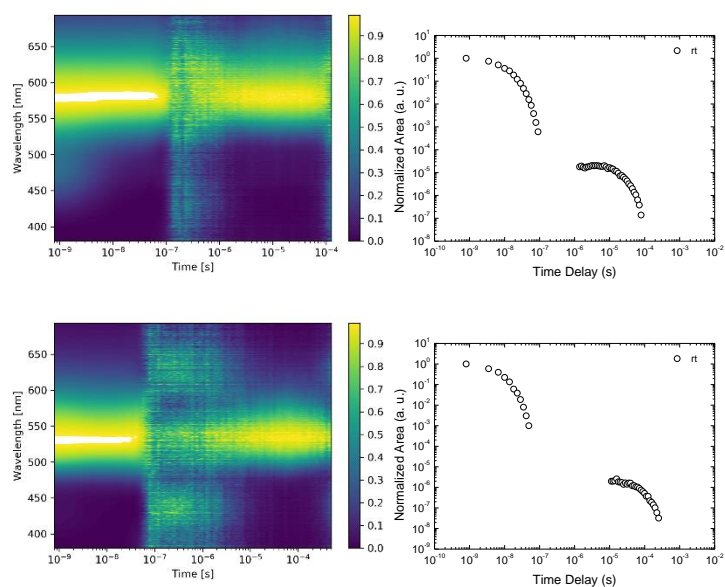


Figure S14: Normalised time-resolved emission spectra for **BTaz-Na-PXZ** in chloroform (top) and toluene (bottom) at room temperature, with the decay of the total emission. Data points without signal have been omitted from the decay.

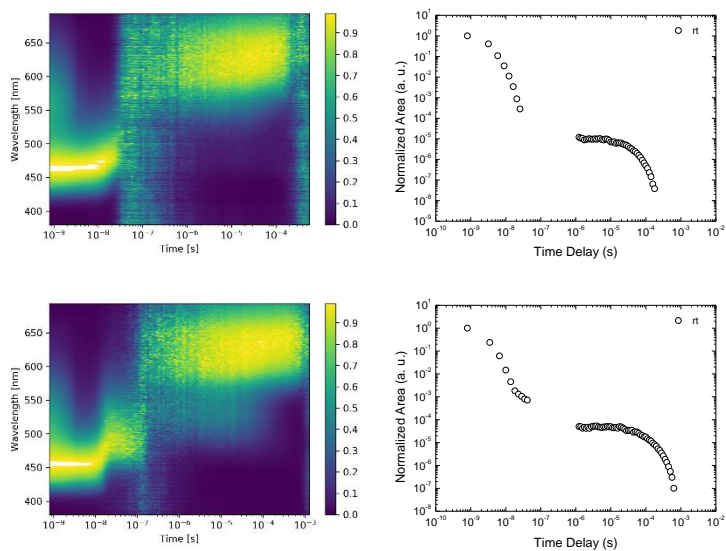


Figure S15: Normalised time-resolved emission spectra for *BTaz-Th-PXZ* in chloroform (top) and toluene (bottom) at room temperature, with the decay of the total emission. Data points without signal have been omitted from the decay.

13. Singlet oxygen generation

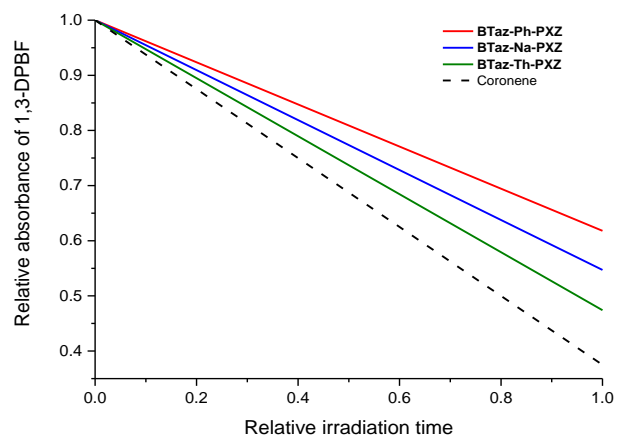


Figure S16: Relative decrease in absorbance of 1,3-diphenylisobenzofuran (1,3-DPBF) at 414 nm under continuous irradiation using a single 325 nm LED in the presence of the respective dyad in toluene. Coronene was used as a standard ($\Phi_{\Delta} = 0.90$ in toluene).

14. NMR spectra

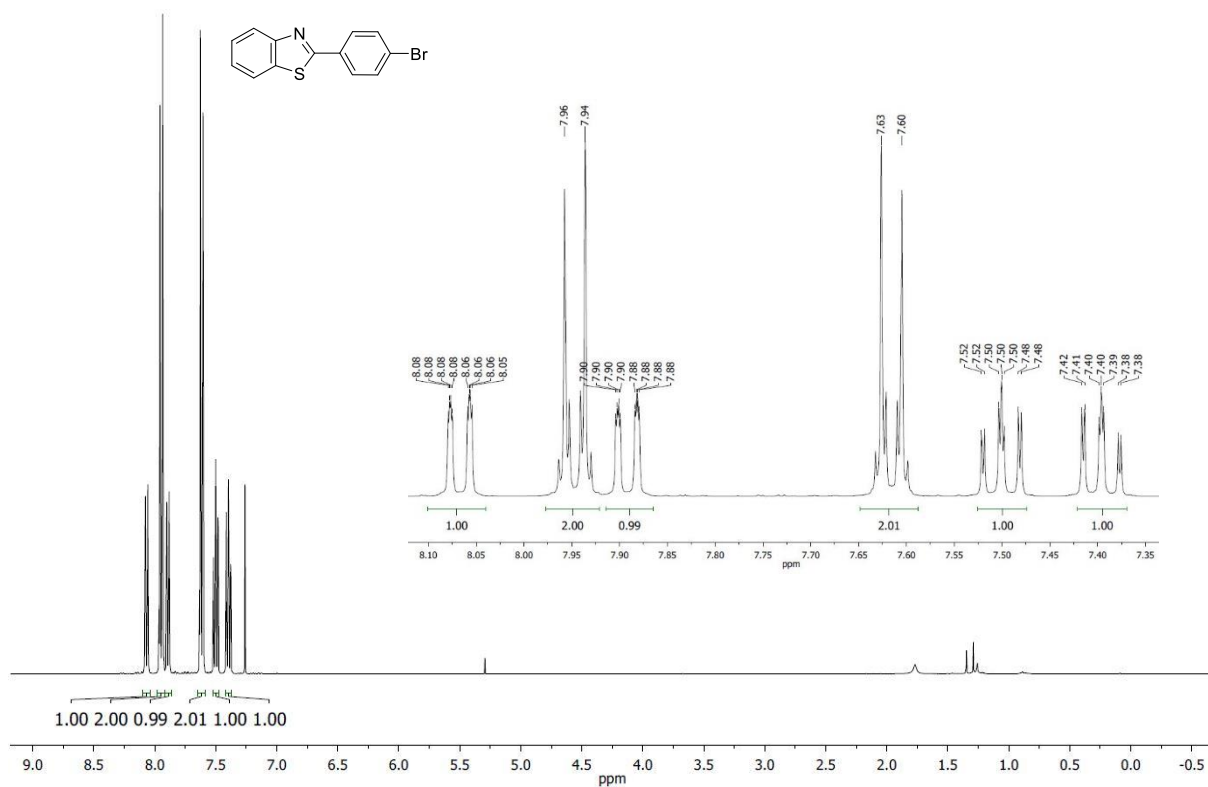


Figure S17: ¹H NMR spectrum of BTaz-Ph in CDCl₃ (400 MHz).

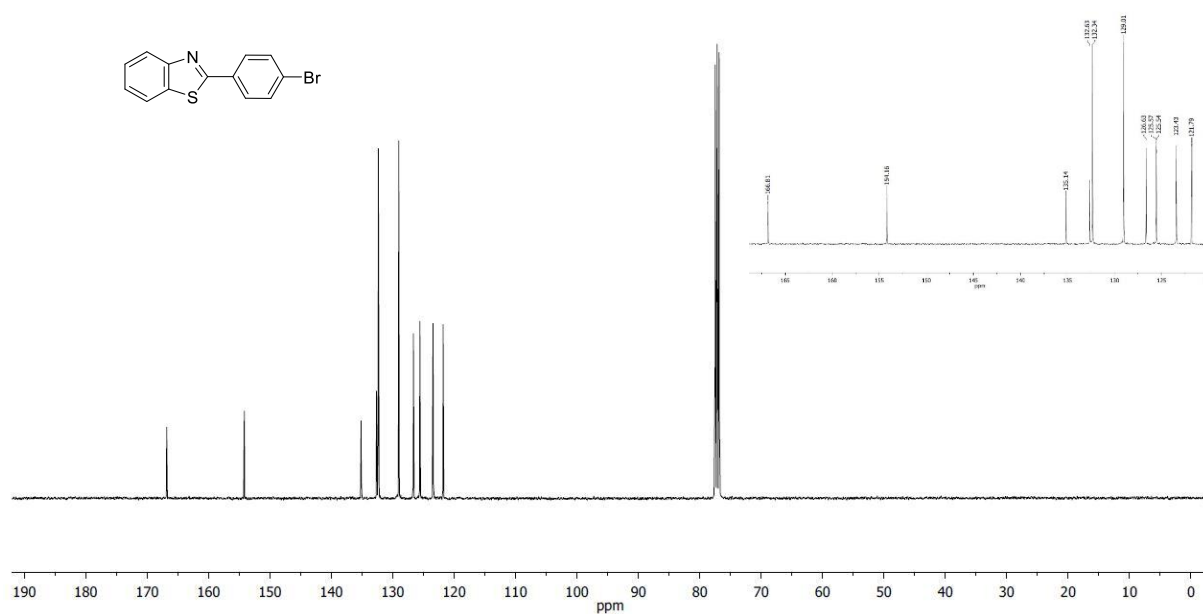


Figure S18: ¹³C NMR spectrum of BTaz-Ph in CDCl₃ (100 MHz).

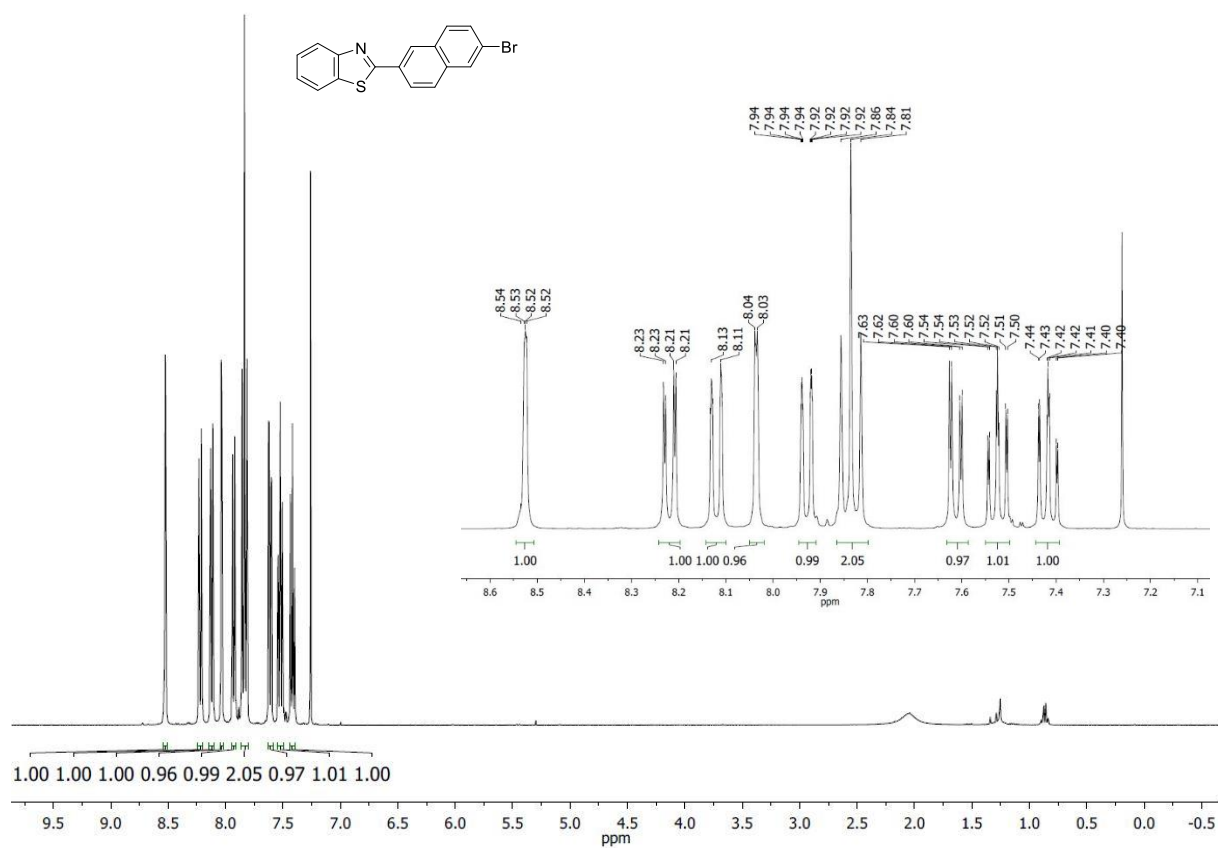


Figure S19: ¹H NMR spectrum of BTaz-Na in CDCl₃ (400 MHz).

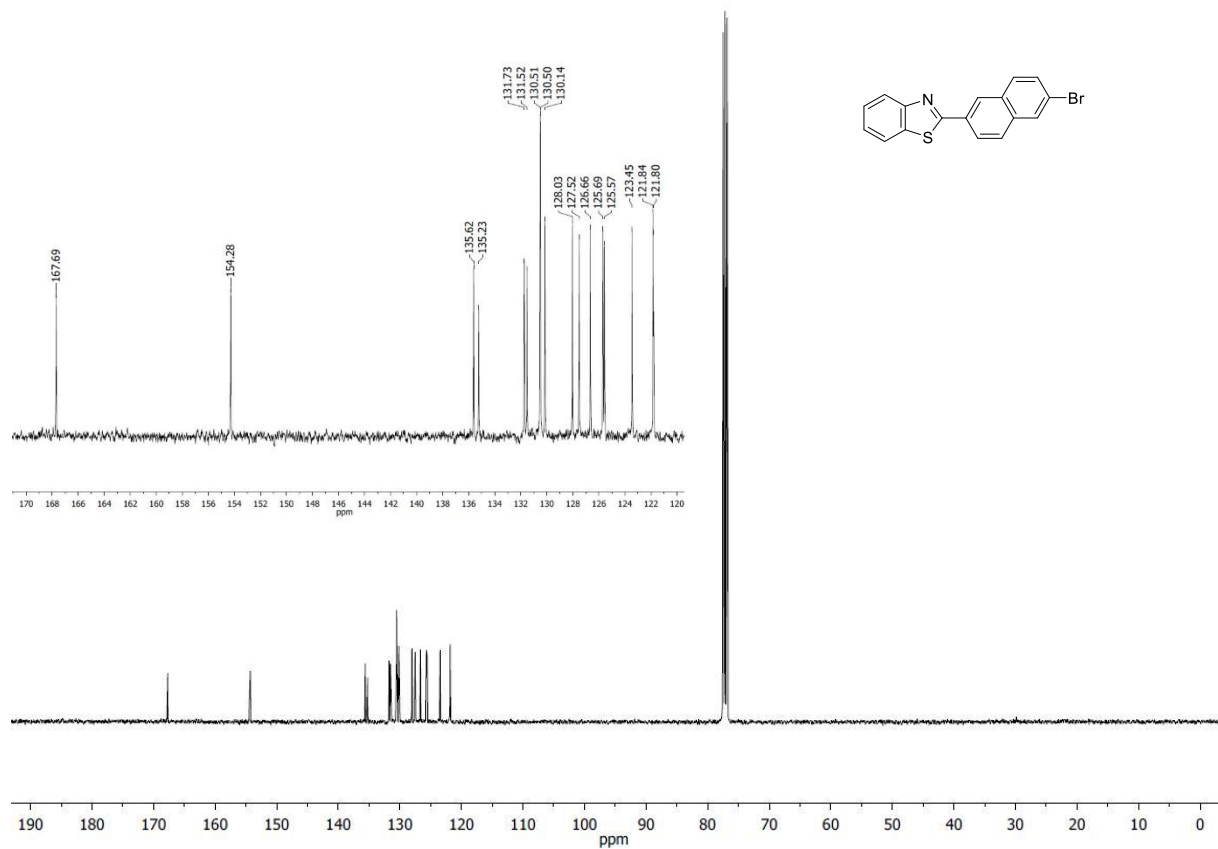


Figure S20: ¹³C NMR spectrum of BTaz-Na in CDCl₃ (100 MHz).

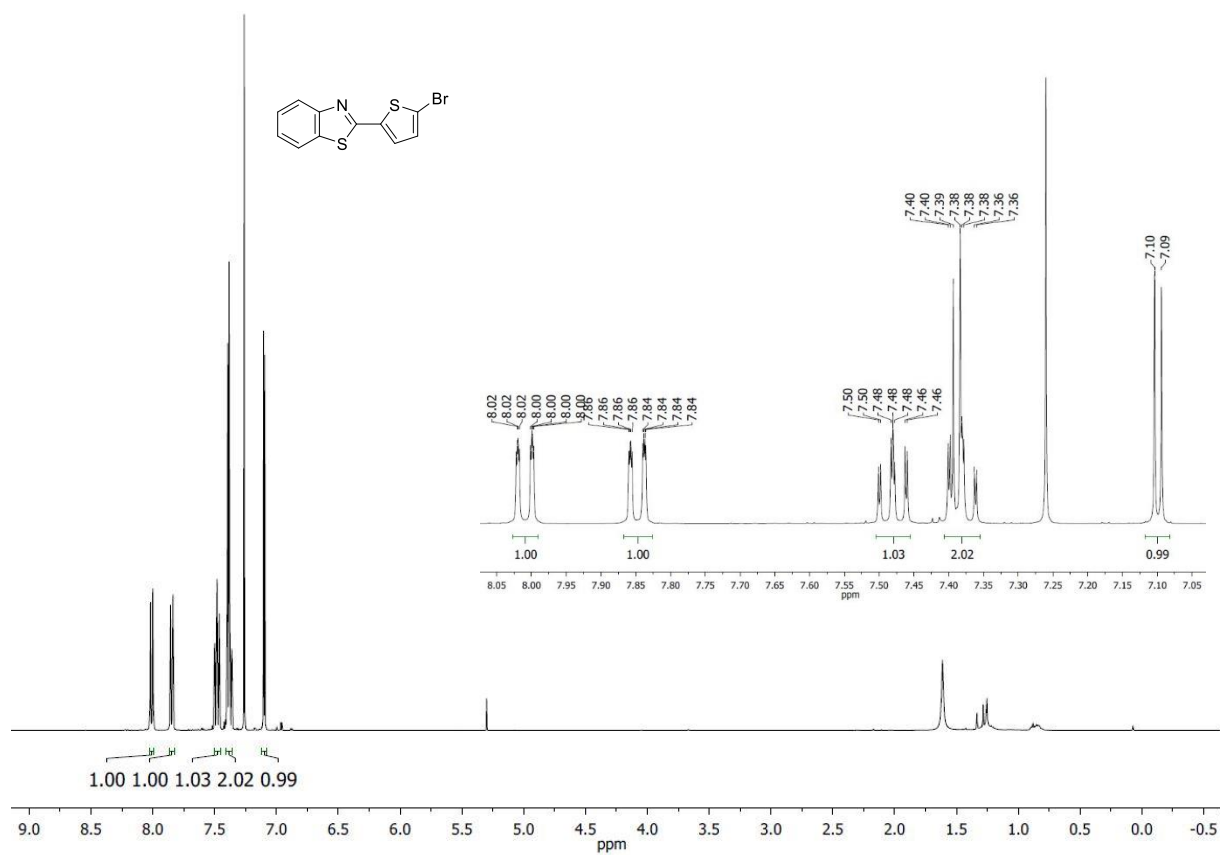


Figure S21: ¹H NMR spectrum of BTaz-Th in CDCl₃ (400 MHz).

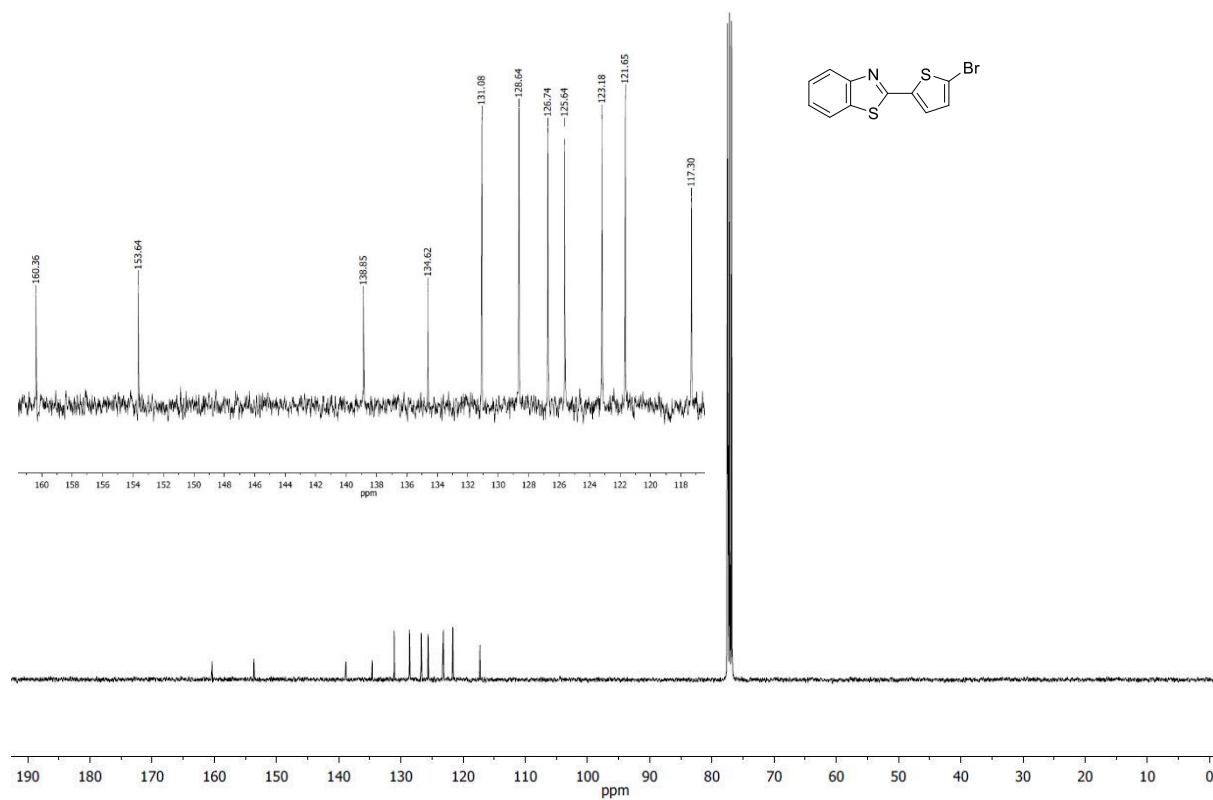


Figure S22: ¹³C NMR spectrum of BTaz-Th in CDCl₃ (100 MHz).

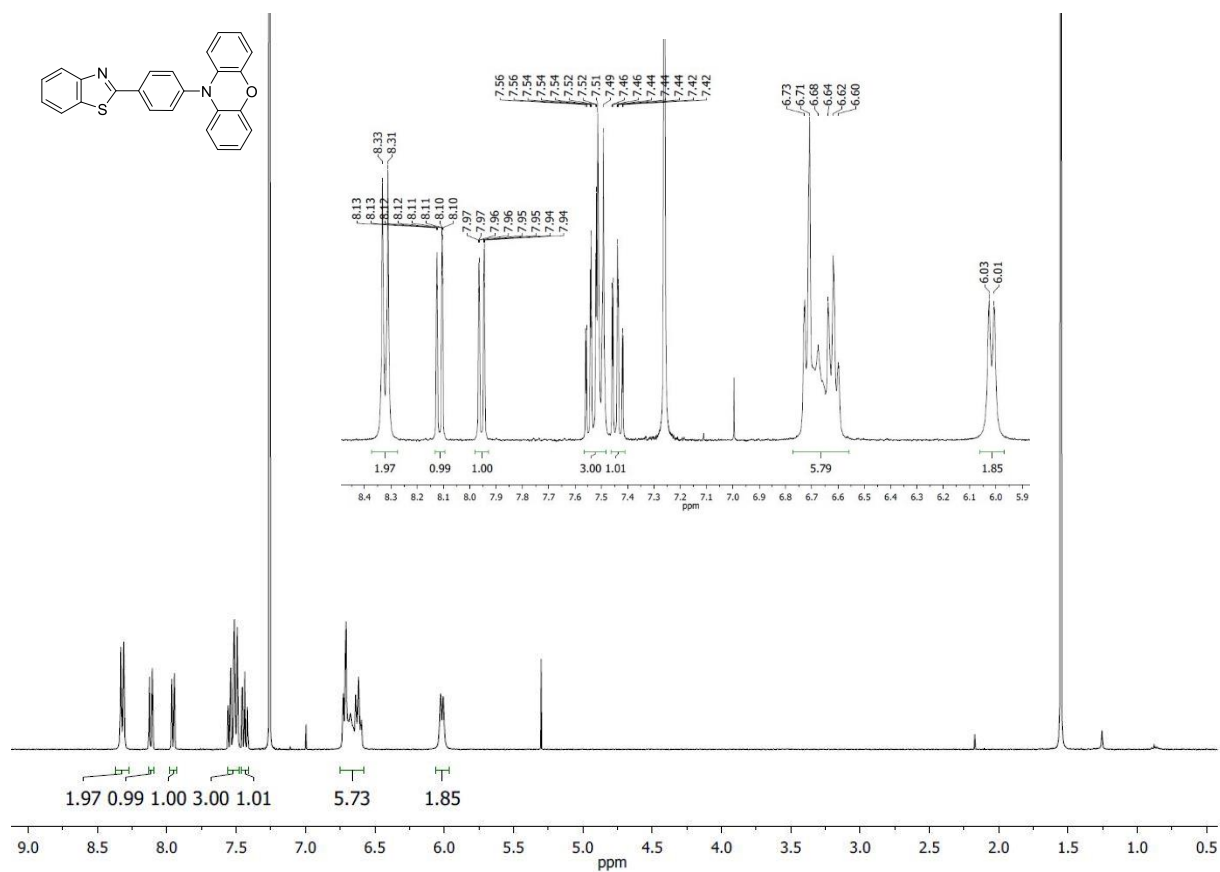


Figure S23: ^1H NMR spectrum of BTaz-Ph-PXZ in CDCl_3 (400 MHz).

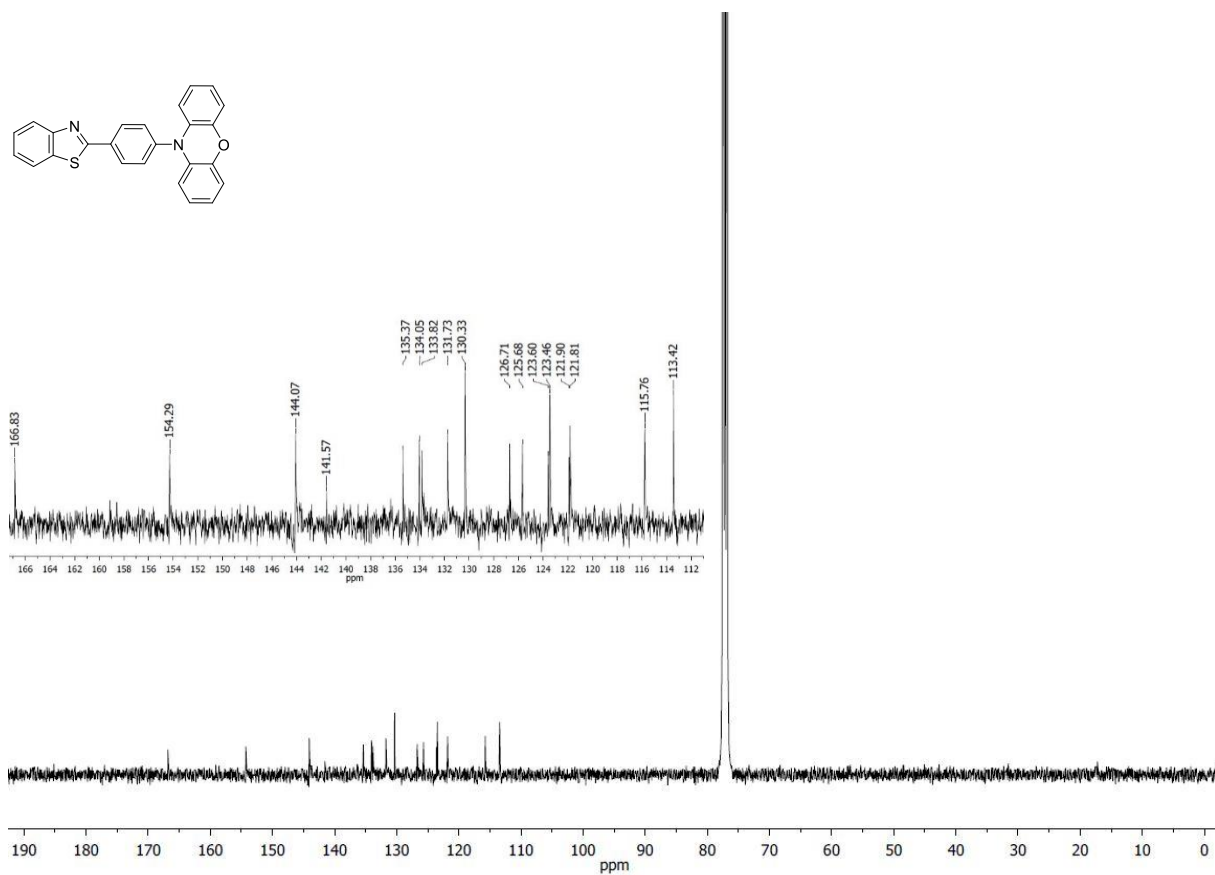


Figure S24: ¹³C NMR spectrum of BTaz-Ph-PXZ in CDCl₃ (100 MHz).

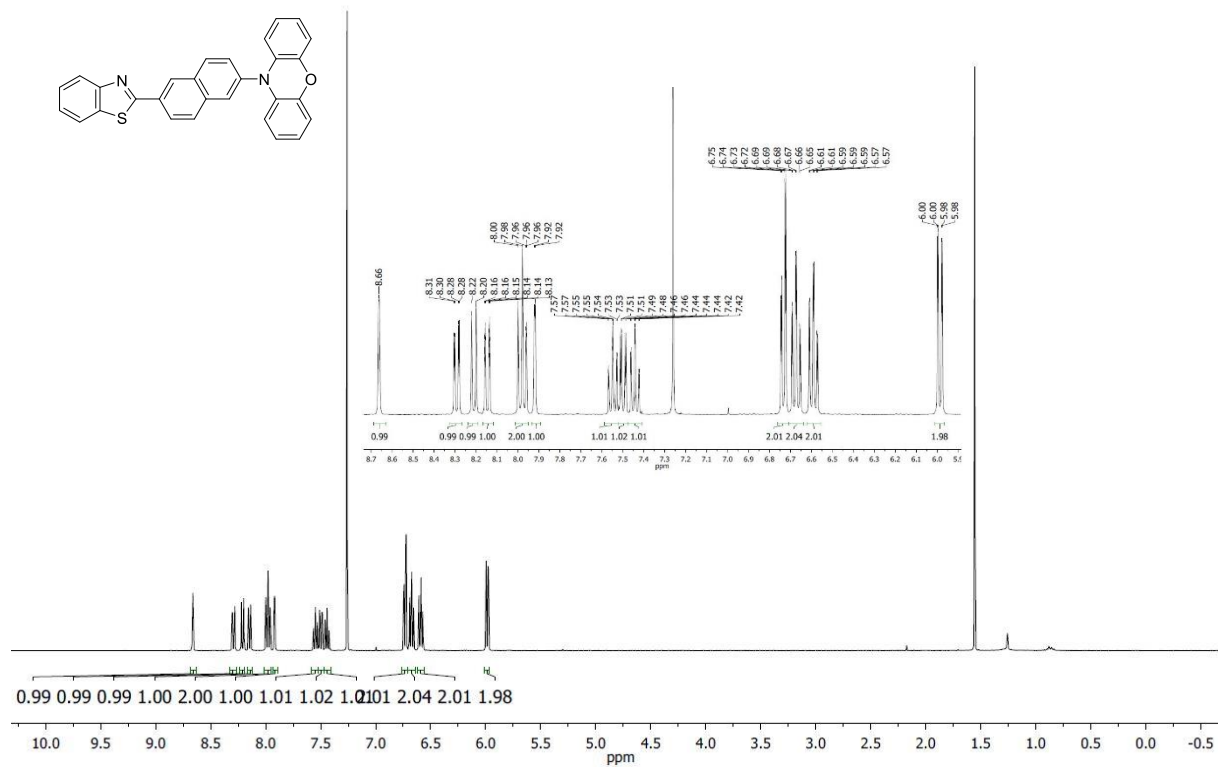


Figure S25: ¹H NMR spectrum of BTaz-Na-PXZ in CDCl₃ (400 MHz).

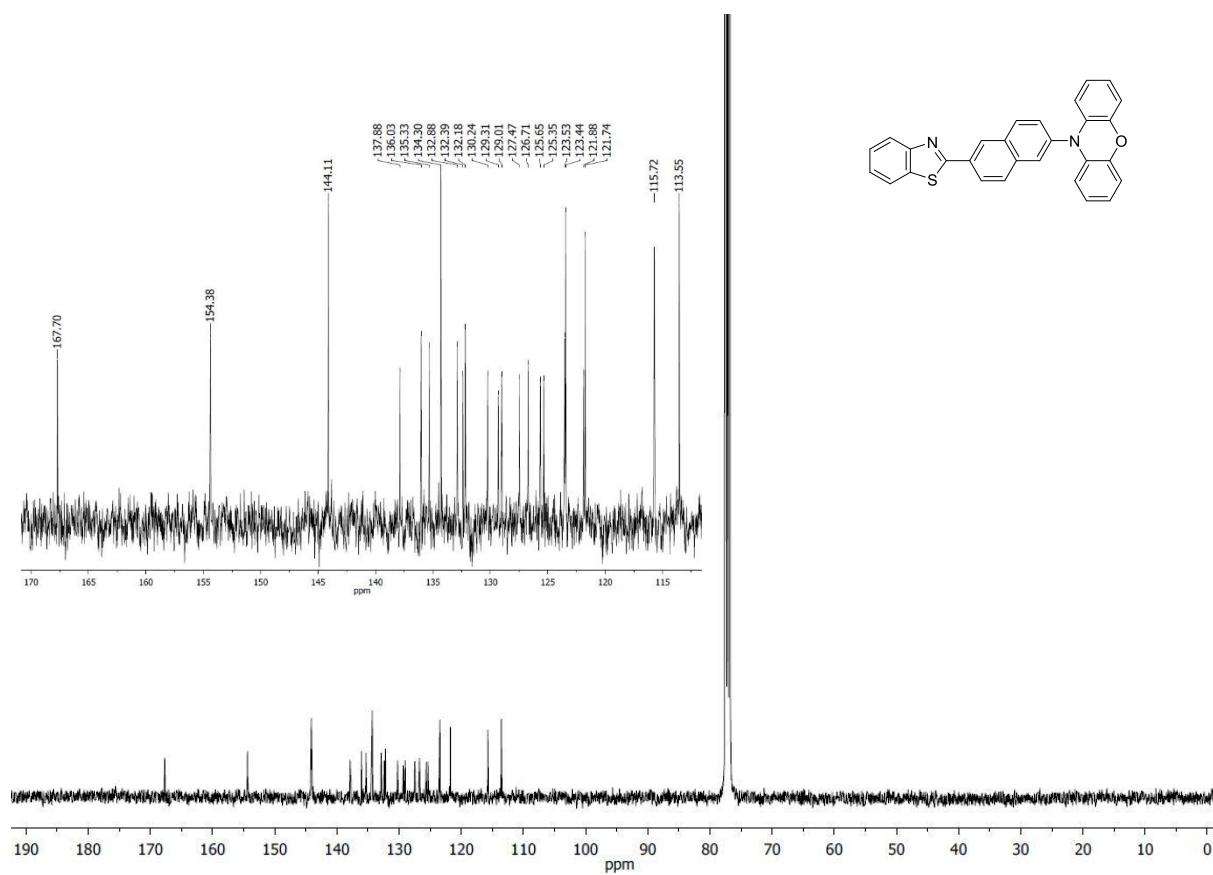


Figure S26: ^{13}C NMR spectrum of BTaz-Na-PXZ in CDCl_3 (100 MHz).

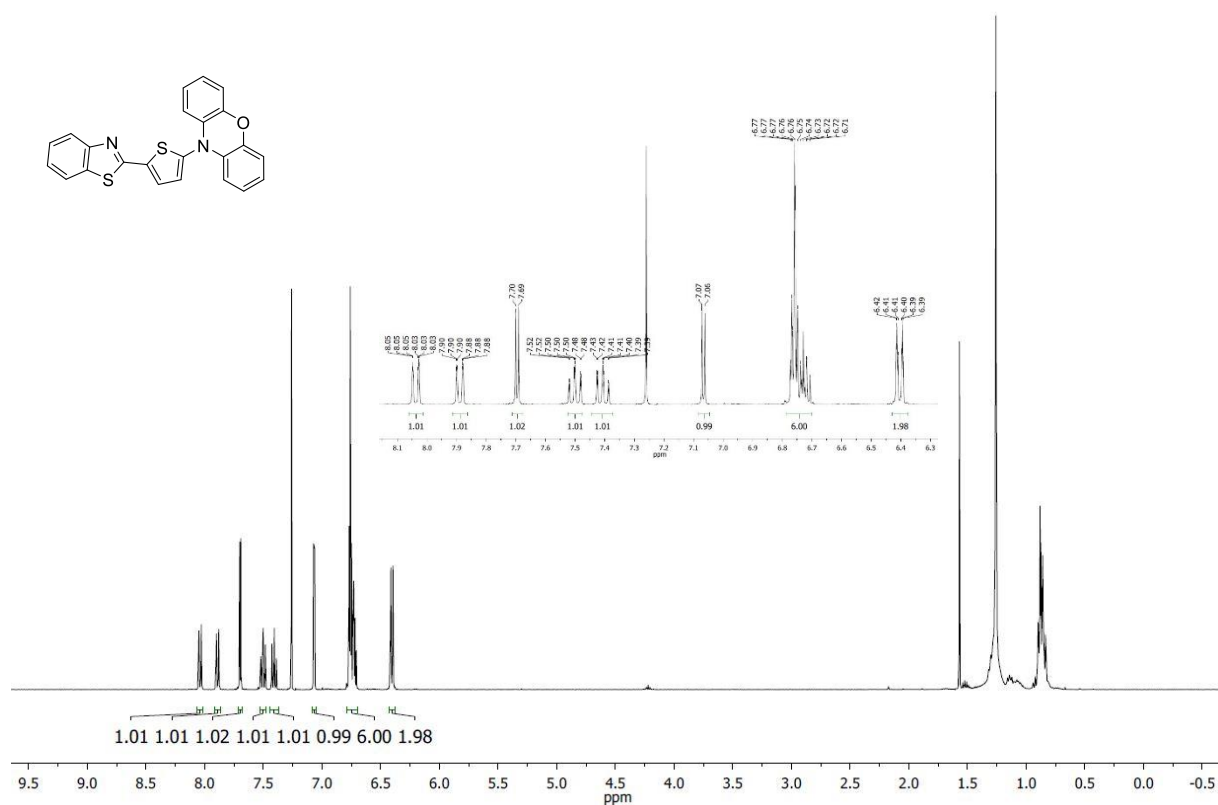


Figure S27: ¹H NMR spectrum of BTaz-Th-PXZ in CDCl₃ (400 MHz).

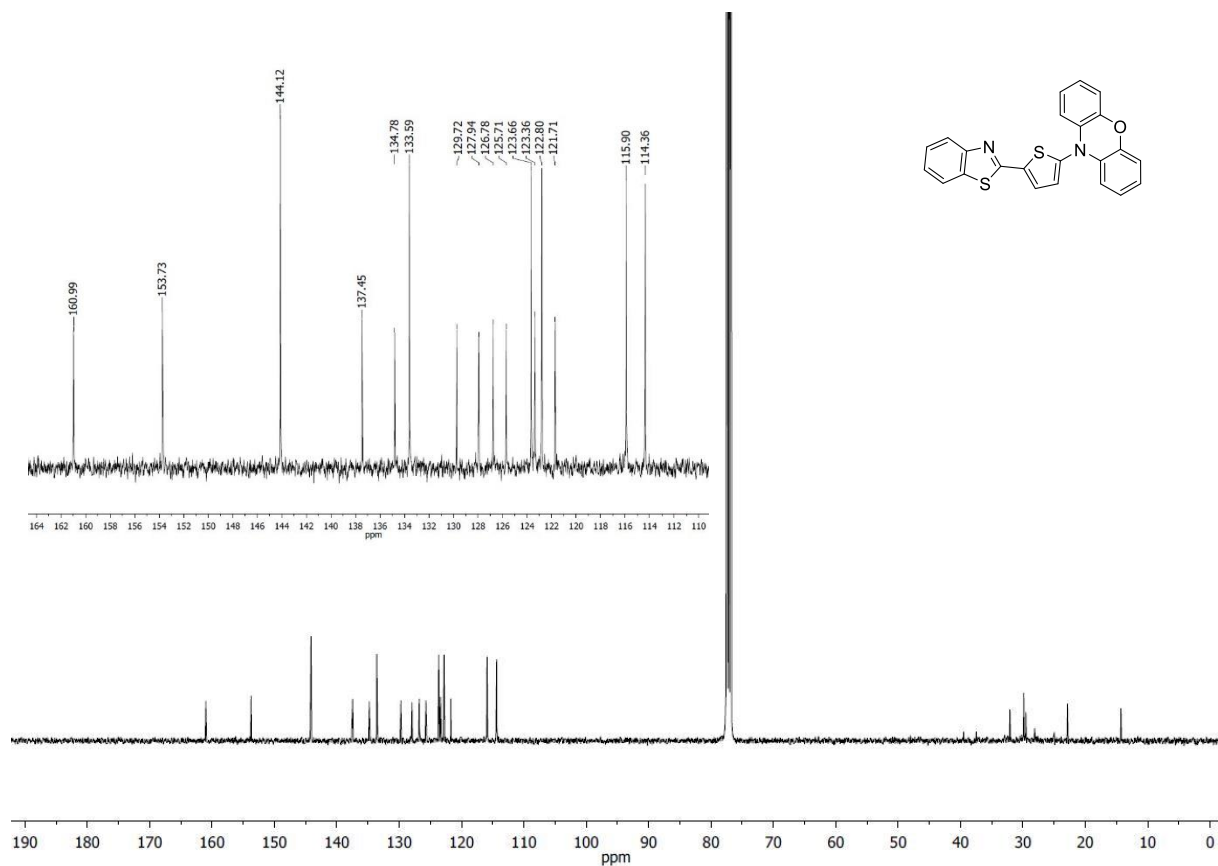


Figure S28: ¹³C NMR spectrum of BTaz-Th-PXZ in CDCl₃ (100 MHz).

15. Coordinates of optimized geometries

BTaz-Ph-PXZ

C	5.46492	-0.00003	-0.65282
C	5.17416	0.00003	0.72402
C	6.22230	0.00008	1.64678
C	7.52220	0.00006	1.18471
C	7.79645	-0.00000	-0.18739
C	6.77461	-0.00005	-1.11909
S	3.97756	-0.00008	-1.55701
C	3.09833	-0.00001	-0.01343
N	3.83917	0.00004	1.04190
C	1.63512	-0.00001	0.02251
C	0.86258	-0.00003	-1.14018
C	-0.51864	-0.00003	-1.06479
C	-1.14689	-0.00000	0.17479
C	-0.38702	0.00002	1.33778
C	0.99434	0.00002	1.26372
C	-2.63531	-2.44438	0.05012
C	-3.37511	-3.61620	-0.06532
C	-4.75607	-3.56853	-0.12044
C	-5.39887	-2.33761	-0.05718
C	-4.66627	-1.17574	0.06639
O	-5.36486	0.00001	0.15599
C	-4.66626	1.17576	0.06637
C	-5.39885	2.33763	-0.05722
C	-4.75604	3.56854	-0.12051
C	-3.37509	3.61620	-0.06539
C	-2.63529	2.44438	0.05007
C	-3.26855	1.20863	0.11943
N	-2.56736	0.00000	0.25413
C	-3.26856	-1.20863	0.11945
H	5.98960	0.00012	2.70849
H	8.34629	0.00010	1.89385
H	8.82898	-0.00001	-0.52821
H	6.99216	-0.00010	-2.18416
H	1.34060	-0.00005	-2.11813
H	-1.12851	-0.00005	-1.96614
H	-0.89732	0.00004	2.29841
H	1.60439	0.00004	2.16262
H	-1.55017	-2.49015	0.09504
H	-2.85501	-4.56960	-0.11183
H	-5.33986	-4.48041	-0.21192
H	-6.48207	-2.25300	-0.09558
H	-6.48205	2.25303	-0.09562
H	-5.33983	4.48042	-0.21200
H	-2.85498	4.56960	-0.11193
H	-1.55015	2.49014	0.09499

BTaz-Na-PXZ

C	-6.75314	0.02211	-0.45419
C	-6.22304	-0.03401	0.84848
C	-7.09265	-0.07112	1.94090
C	-8.45362	-0.05130	1.71583
C	-8.96601	0.00494	0.41503
C	-8.12447	0.04197	-0.68150
S	-5.44944	0.05878	-1.60628
C	-4.31007	-0.00440	-0.24422
N	-4.85337	-0.04707	0.92490
C	-0.62005	-0.02531	0.44384
C	-0.07834	0.00612	-0.87142

C	1.32426	0.01146	-1.03573
C	2.15174	-0.01215	0.05263
C	1.61732	-0.04339	1.36086
C	0.26510	-0.05025	1.54937
C	3.65937	-2.44314	0.11207
C	4.41269	-3.60835	0.20317
C	5.79441	-3.55113	0.18422
C	6.42456	-2.31719	0.07195
C	5.67762	-1.16215	-0.02829
O	6.35869	0.01818	-0.17665
C	5.66167	1.18557	-0.00202
C	6.39301	2.34800	0.12426
C	5.74634	3.57031	0.26573
C	4.36405	3.60811	0.28798
C	3.62643	2.43520	0.17047
C	4.26316	1.20846	0.02032
N	3.56430	-0.00143	-0.12683
C	4.27958	-1.20462	-0.00750
C	-0.96640	0.03182	-1.97008
C	-2.31787	0.02788	-1.77925
C	-2.86564	-0.00222	-0.47389
C	-2.01724	-0.02906	0.61064
H	-6.67668	-0.11464	2.94417
H	-9.13958	-0.07956	2.55889
H	-10.04247	0.01976	0.26233
H	-8.52628	0.08563	-1.69067
H	1.75734	0.03617	-2.03465
H	2.30666	-0.06133	2.20315
H	-0.15392	-0.07403	2.55387
H	2.57372	-2.49615	0.12368
H	3.90280	-4.56453	0.28946
H	6.38845	-4.45818	0.25587
H	7.50765	-2.22533	0.05127
H	7.47722	2.27124	0.10073
H	6.32810	4.48347	0.35772
H	3.84129	4.55487	0.39775
H	2.54022	2.47328	0.18563
H	-0.55423	0.05503	-2.97732
H	-2.97813	0.04742	-2.64424
H	-2.44377	-0.05241	1.61140

BTaz-Th-PXZ

C	-5.26642	-0.00004	0.33745
C	-4.60584	0.00005	-0.90562
C	-5.35884	0.00012	-2.08138
C	-6.73624	0.00011	-1.99596
C	-7.37869	0.00003	-0.75359
C	-6.65319	-0.00005	0.42422
S	-4.08863	-0.00012	1.62232
C	-2.82031	-0.00002	0.38004
N	-3.23435	0.00005	-0.84208
C	-1.42693	-0.00004	0.75838
C	-0.87697	-0.00007	2.01378
C	0.53316	-0.00006	1.99847
C	1.04583	-0.00002	0.73474
S	-0.21206	0.00000	-0.48043
C	2.45148	-2.45060	0.28920
C	3.13784	-3.62533	0.00729
C	4.43245	-3.57687	-0.47838
C	5.04019	-2.34460	-0.68236
C	4.35868	-1.17713	-0.40309
O	5.02384	0.00003	-0.62132
C	4.35867	1.17717	-0.40305

C	5.04015	2.34466	-0.68228
C	4.43240	3.57692	-0.47824
C	3.13779	3.62534	0.00743
C	2.45145	2.45059	0.28929
C	3.05071	1.21373	0.08762
N	2.39244	-0.00001	0.36925
C	3.05072	-1.21372	0.08757
H	-4.84195	0.00019	-3.03746
H	-7.33208	0.00017	-2.90533
H	-8.46516	0.00002	-0.71074
H	-7.15626	-0.00011	1.38788
H	-1.47126	-0.00009	2.92326
H	1.16691	-0.00008	2.88015
H	1.43518	-2.49075	0.67303
H	2.64673	-4.58074	0.17239
H	4.97560	-4.49122	-0.70117
H	6.05503	-2.26089	-1.06298
H	6.05500	2.26098	-1.06290
H	4.97554	4.49128	-0.70100
H	2.64667	4.58074	0.17256
H	1.43515	2.49071	0.67313