Photodynamics of Zr-Based MOFs: Effect of Explosive Nitroaromatics

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Figure S1. Comparison of the X-Rays diffraction patterns of Zr-NDC and Zr-NDC/CN MOFs. The one of Zr-NDC* was taken from Ref 1.



Figure S2. UV-visible absorption spectra of Zr-NDC/Tz in ACN suspension without and with different amounts (0, 5, 10, 20, 30, 50, 75, 100, 200 and 500 ppm) of (A) nitrobenzene (NB), (B) nitrotoluene (NT), (C) dinitrobenzene (DNB), (D) dinitrotoluene (DNT) and (E) trinitrobenzene (TNB).



Figure S3. UV-visible absorption spectra of the nitroaromatic molecules (NB, NT, DNB, DNT and TNB) dissolved in ACN.



Figure S4. Magic-angle emission decays of Zr-NDC/Tz without (blue opened circles) and containing 500 ppm of NT (red opened circles) upon excitation at 371 nm and observation at 400 and 550 nm, respectively. The solid lines are from the best-fit using a multiexponential function.



Figure S5. Magic-angle emission decays of Zr-NDC/Tz without (blue opened circles) and containing 500 ppm of DNB (red opened circles) upon excitation at 371 nm and observation at 400 and 550 nm, respectively. The solid lines are from the best-fit using a multiexponential function.



Figure S6. Magic-angle emission decays of Zr-NDC/Tz without (blue opened circles) and containing 500 ppm of DNT (red opened circles) upon excitation at 371 nm and observation at 400 and 550 nm, respectively. The solid lines are from the best-fit using a multiexponential function.



Figure S7. Magic-angle emission decays of Zr-NDC/Tz without (blue opened circles) and containing 500 ppm of TNB (red opened circles) upon excitation at 371 nm and observation at 400 and 550 nm, respectively. The solid lines are from the best-fit using a multiexponential function.



Figure S8. (A) UV-visible absorption spectra of Zr-NDC/Tz in ACN suspension without and upon addition of different amounts (expressed in ppm) of TNP. (B) UV-visible absorption spectra of different concentrated (expressed in ppm) solutions of TNP in ACN.



Figure S9. Spectral overlap between the absorption spectrum of TNP in ACN (black line) and the emission spectrum of the Zr-NDC/Tz MOF suspended in ACN (red line).



Figure S10. Time-resolved transient spectra of Zr-NDC/Tz in ACN (lower part) at 100 ns delay, and excitation at 355 nm. The upper part displays the decays of Zr-NDC/Tz without and with 200 ppm of TNP. The excitation wavelength was 355 nm, and the observation ones were 500 and 600 nm, respectively. The solid lines are from the best multiexponential fits.



Figure S11. Spectral overlap between the absorption spectrum of TNP in ACN (black line) and the emission spectrum of Zr-NDC/CN MOF suspended in ACN (red line).



Figure S12. Time-resolved transient spectra of Zr-NDC/CN in ACN (lower part), upon excitation at 355 nm and gating at 100 ns. The upper part displays the decays of Zr-NDC/CN without and with 200 ppm of TNP. The observation ones were 500 and 600 nm, respectively. The solid lines are from the best multiexponential fits.

Table S1. Values of time constants (τ i), normalized (to 100) pre-exponential factors (ai) and fractional contributions (ci= τ i·ai) obtained from the fit of the emission decays of Zr-NDC/Tz in presence of 500 ppm of NB in an ACN suspension upon excitation at 371 nm and observation as indicated. The error estimation is provided by the fluofit analysis of the decay.

| Sample | λObs | τ1 / ps ±50 | a 1 | C 1 | τ ₂ / ns ±0.2 | a 2 | C 2 | τ3 / ns ±0.4 | a 3 | C 3 |
|---|------|----------------|------------|------------|-----------------------------|------------|------------|-----------------|------------|------------|
| Zr-NDC/Tz + 500 ppm NB λex = 371 nm | 400 | 440 | 62 | 15 | 2.5 | 30 | 41 | 10.1 | 8 | 44 |
| | 430 | 440 | 56 | 10 | 2.5 | 29 | 29 | 10.1 | 15 | 61 |
| | 450 | 440 | 52 | 8 | 2.5 | 29 | 25 | 10.1 | 19 | 67 |
| | 500 | 440 | 28 | 2 | 2.5 | 28 | 13 | 10.1 | 44 | 85 |
| | 550 | 440 | 14 | 1 | 2.5 | 28 | 11 | 10.1 | 58 | 88 |

Table S2. Values of time constants (τ i), normalized (to 100) pre-exponential factors (ai) and fractional contributions (ci= τ i·ai) obtained from the fit of the emission decays of Zr-NDC/Tz in presence of 500 ppm of NT in an ACN suspension upon excitation at 371 nm and observation as indicated. The error estimation is provided by the fluofit analysis of the decay.

| Sample | λObs | τ1 / ps ±50 | a 1 | C 1 | τ2 / ns ±0.2 | a 2 | C 2 | τ3 / ns ±0.4 | a 3 | C 3 |
|---|------|----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| Zr-NDC/Tz + 500 ppm NT λex = 371 nm | 400 | 450 | 64 | 20 | 2.5 | 33 | 58 | 10.0 | 3 | 21 |
| | 430 | 450 | 59 | 13 | 2.5 | 32 | 41 | 10.0 | 9 | 46 |
| | 450 | 450 | 49 | 7 | 2.5 | 31 | 26 | 10.0 | 20 | 67 |
| | 500 | 450 | 24 | 2 | 2.5 | 29 | 13 | 10.0 | 47 | 85 |
| | 550 | 450 | 10 | 1 | 2.5 | 29 | 10 | 10.0 | 61 | 89 |

Table S3. Values of time constants (τ i), normalized (to 100) pre-exponential factors (ai) and fractional contributions (ci= τ i·ai) obtained from the fit of the emission decays of Zr-NDC/Tz in presence of 500 ppm of DNB in an ACN suspension upon excitation at 371 nm and observation as indicated. The error estimation is provided by the fluofit analysis of the decay.

| Sample | λObs | τ1 / ps ±50 | a 1 | C 1 | τ ₂ / ns ±0.2 | a 2 | C 2 | τ3 / ns ±0.4 | a 3 | C 3 |
|--|------|----------------|------------|------------|-----------------------------|------------|------------|-----------------|------------|------------|
| Zr-NDC/Tz + 500 ppm DNB λex = 371 nm | 400 | 450 | 65 | 22 | 2.6 | 33 | 63 | 10.2 | 2 | 15 |
| | 430 | 450 | 61 | 16 | 2.6 | 33 | 49 | 10.2 | 6 | 35 |
| | 450 | 450 | 53 | 9 | 2.6 | 31 | 30 | 10.2 | 16 | 61 |
| | 500 | 450 | 30 | 3 | 2.6 | 28 | 14 | 10.2 | 42 | 83 |
| | 550 | 450 | 15 | 1 | 2.6 | 28 | 11 | 10.2 | 57 | 8 |

Table S4. Values of time constants (τ i), normalized (to 100) pre-exponential factors (ai) and fractional contributions (ci= τ i·ai) obtained from the fit of the emission decays of Zr-NDC/Tz in presence of 500 ppm of DNT in an ACN suspension upon excitation at 371 nm and observation as indicated. The error estimation is provided by the fluofit analysis of the decay.

| Sample | λObs | τ ₁ / ps ±50 | a 1 | C 1 | τ ₂ / ns ±0.2 | a ₂ | C 2 | τ ₃ / ns ±0.4 | a 3 | C 3 |
|--|------|----------------------------|------------|------------|-----------------------------|-----------------------|------------|-----------------------------|------------|------------|
| Zr-NDC/Tz + 500 ppm DNT λex = 371 nm | 400 | 430 | 63 | 18 | 2.4 | 32 | 50 | 9.9 | 5 | 32 |
| | 430 | 430 | 59 | 13 | 2.4 | 32 | 40 | 9.9 | 9 | 47 |
| | 450 | 430 | 48 | 7 | 2.4 | 31 | 24 | 9.9 | 21 | 69 |
| | 500 | 430 | 25 | 2 | 2.4 | 30 | 14 | 9.9 | 45 | 84 |
| | 550 | 430 | 10 | 1 | 2.4 | 28 | 10 | 9.9 | 62 | 89 |

Table S5. Values of time constants (τ i), normalized (to 100) pre-exponential factors (ai) and fractional contributions (ci= τ i·ai) obtained from the fit of the emission decays of Zr-NDC/Tz in presence of 500 ppm of TNB in an ACN suspension upon excitation at 371 nm and observation as indicated. The error estimation is provided by the fluofit analysis of the decay.

| Sample | λObs | τ1 / ps ±50 | a 1 | C 1 | τ ₂ / ns ±0.2 | a 2 | C 2 | τ3 / ns ±0.4 | a 3 | C 3 |
|--|------|----------------|------------|------------|-----------------------------|------------|------------|-----------------|------------|------------|
| Zr-NDC/Tz + 500 ppm TNB λex = 371 nm | 400 | 450 | 63 | 19 | 2.6 | 34 | 60 | 10.2 | 3 | 21 |
| | 430 | 450 | 59 | 13 | 2.6 | 32 | 41 | 10.2 | 9 | 46 |
| | 450 | 450 | 48 | 7 | 2.6 | 32 | 27 | 10.2 | 20 | 66 |
| | 500 | 450 | 24 | 2 | 2.6 | 30 | 14 | 10.2 | 46 | 84 |
| | 550 | 450 | 10 | 1 | 2.6 | 29 | 11 | 10.2 | 61 | 88 |

Table S6. Values of the time constants obtained from the fit of the μ s-transients of Zr-NDC/Tz without and in presence of 200 ppm of TNP in ACN suspension.

| Sample | λObs | τ_1 / ns | $\tau_2 / \mu s$ |
|---|------|---------------|------------------|
| | 500 | 450 ± 40 | 2.0 ± 0.3 |
| Zr-NDC/Tz λex = 355 nm | 600 | 450 ± 40 | 2.0 ± 0.3 |
| | 700 | - | 2.0 ± 0.3 |
| Zr-NDC/Tz | 500 | 20 ± 5 | 1.0 ± 0.2 |
| +200 ppm TNP $\lambda ex = 355 \text{ nm}$ | 600 | - | 1.0 ± 0.2 |
| | 700 | - | 1.0 ± 0.2 |

Table S7. Values of the HOMO and LUMO energy levels and the band gap of the nitroderivative molecules (NB, NT, DNB, DNT, TNB and TNP). The geometry, electronic structures and HOMO and LUMO orbital energies of NT and TNB were calculated by using the hybrid B3LYP functional of density functional theory (DFT) and 6-31G* basis set.²

| Sample | HOMO (eV) | LUMO (eV) | Band Gap (eV) |
|--------|-----------|-----------|---------------|
| NB* | -7.59 | -2.43 | 5.16 |
| NT | -7.27 | -2.36 | 4.91 |
| DNB* | -7.99 | -3.43 | 4.56 |
| DNT* | -7.76 | -3.22 | 4.54 |
| TNB | -8.93 | -3.68 | 5.25 |
| TNP* | -8.24 | -3.90 | 4.34 |

*These values were taken from Ref 3.

Table S8. Values of the time constants obtained from the fit of the µs-transients of Zr-NDC/CN without and in presence of 200 ppm of TNP in ACN suspension.

| Sample | λobs | τ_1 / ns | τ2 / μs |
|-------------------------------|------|---------------|---------------|
| | 500 | 480 ± 40 | 2.3 ± 0.3 |
| Zr-NDC/CN λex = 355 nm | 600 | 480 ± 40 | 2.3 ± 0.3 |
| | 700 | - | 2.3 ± 0.3 |
| Zr-NDC/CN | 500 | 12 ± 5 | 1.1 ± 0.2 |
| +200 ppm TNP | 600 | - | 1.1 ± 0.2 |
| $\lambda ex = 355 \text{ nm}$ | 700 | - | 1.1 ± 0.2 |

I. Synthesis and Characterization of the MOFs

¹H and ¹³C-NMR spectra of naphthalene-linkers were performed in a Bruker Avance 300 MHz spectrometer (Larmor frecuencies of 300 MHz). The used solvents for NMR spectra were CDCl₃ or DMSO-d₆. Fourier Transform Infrared Spectra (FTIR) of all compounds and materials were recorded on a Perkin-Elmer RX-1 instrument and are reported in terms of the frequency of absorption (cm^{-1}) using the KBr pellets technique (about 1 mg of sample and 300 mg of dry KBr were used in the preparation of pellets). Thermogravimetric analysis (TGA) data were obtained on a TA Q-500 analyzer under air atmosphere, using approximately 5 mg of sample under a flow of 60 mL/min. The samples were heated from 40 to 850 °C at 10 °C/min. Specific surface area measurements and porosity analysis were performed using N₂ adsorption isotherms (Micromeritics, ASAP 2020 MICROPORE DRY Analyzer) using the BET method for surface area calculation. X-Ray Diffraction (XRD) **patterns** were performed using a Bruker D8 diffractometer with a Sol-X energy dispersive detector, working at 40 kV and 30 mA and employing CuK α ($\lambda = 1.5418$ Å) filtered radiation. The diffractograms were recorded using a step size of 0.02° and exposure time of 0.5 s per step and a 2θ range of 2-40°. The textural properties were analyzed by N₂ adsorption/desorption experiments performed at -196 °C using a static volumetric apparatus, Micromeritics ASAP 2010 analyzer. The samples (150-200 mg) were outgassed, previous to the analysis, for 12 h at 80 °C, or till the outgassing pressure reached 5 mm Hg. For the analysis at low relative pressure range, up to $P/P_0 = 0.05$, successive doses of nitrogen of 4 cm³ STP/g were added, equilibrating for 1.5 h. Subsequently, the adsorption branch of the isotherm was obtained following a previously fixed 40-points P/P0 table, and the desorption branch following a previously fixed 20-points P/P0 table. The specific total surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Ref 4). atmosphere and a heating rate of 10 °C min⁻¹. Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi Model SU- 8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface.

1- General scheme for synthesis of linkers and MOFs

The preparation of linkers and their corresponding MOFs are described in following scheme: The desired linker 4-cyano-2,6-naphthalendicarboxylic acid (NDC-COOH/CN) was prepared starting from dimethyl 2,6-naphthalenedicarboxilate (NDC) in three successive step, 1: selective 4-monobromination (KAc/Br₂); 2: nucleophilic substitution of bromine by an cyano group (CuCN/DMF) and finally 3: the saponification of esters groups to obtain free carboxylic acids (NaOH/THF/H₂O) that was purified for recrystallization from (AcOH/MeOH).

The corresponding MOF-NDC/CN (step 4) was prepared following a hydrothermal method previously described before by us from a mixture of 2,6-naphthalendicarboxylic acid, 4-cyano-2,6-naphthalendicarboxylic acid (NDC-COOH/CN)(60:40, molar ratio), ZrCl₄ in

DMF using acetic acid as a modulator. The transformation of cyano group to a tetrazolyl groups (step)5 on the surface of prepared MOFs was done for treatment with sodium azide (NaN₃) at 110°C in dried DMF to give Zr-NDC/Tz that was successive washed with DMF, THF (2x 24h), methanol and ethyl ether and dried "in vacuo".



1.1 Synthesis of Dimethyl 4-bromo-2,6-naphthalenedicarboxylate (NDC/Br)



In a round-bottom flask of 100 mL, 4.88 g of dimethyl 2,6-naphthalenedicarboxylate (19.98 mmol, 1 eq) and 2.94 g of potassium acetate (30.0 mmol, 1.5 eq) were dissolved in 30 mL of acetic acid. Then, 6.2 mL of bromine (120 mmol, 6.0 eq) was added dropwise. The reaction mixture was stirring at room temperature overnight. Then, an additional portion of bromine was added (3.1 mL, 3.0 eq) and keeping the reaction at room temperature 24h. The reaction was monitored by TLC (Heptane/Ethyl Acetate 1:1). After the ending of the reaction the mixture was quenched with a saturated solution of NaHSO₃ and the aqueous phase was extracted twice with dichloromethane (2x250mL). The combined organic phase was washed with distilled water and with brine and dried over anhydrous sodium sulfate. After removing the organic solvent, the crude solid was recrystallized from acetic acid.

¹H NMR (300 MHz, Chloroform-d) δ 8.94 (s, 1H), 8.54 (s, 1H), 8.38 (d, J = 1.5 Hz, 1H), 8.15 (dd, J = 8.6, 1.5 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 4.01 (s, 3H), 3.99 (s, 3H).m/z= theoretical 321.98, found 322.1. Similar protocol described in Ref 5.



Figure S13: FTIR spectrum of dimethyl 4-bromo-2,6-naphthalendicarboxylate (NDC/Br) in KBr.



Figure S14: ¹H-NMR spectrum of dimethyl 4-bromo-2,6-naphthalendicarboxylate (NDC/Br) in Cl₃CD.



1.2 Synthesis of Dimethyl 4-cyano-2,6-naphthalenedicarboxylate (NDC/CN)

In a round-bottom flask of 50 mL, 2.00 g of NDC/Br (6.19 mmol, 1 eq) was dissolved in 15 mL of dried DMF. To prevent side-reactions, the organic mixture was bubbled with argon gas and 665 mg of CuCN (7.43 mmol, 1.2 eq) was added. The reaction mixture was initially heated at 140°C during 24h. The reaction mixture was monitored by TLC (Heptane/AcOEt 2:1). After this period, a second fraction of cupper salt was added 110 mg (1.24 mmol, 0.2 eq) keeping the reaction temperature to 140°C. After 24h, the reaction (monitored by TLC) was completed. In order to remove the excess of cupper salt, 20 mL of distilled water and 1.20 g of KCN was added. The reaction mixture was heated up to 50°C during 2-4h. Then the product was recuperated by filtration and dried. The solid was recrystallized in a mixture AcOH/methanol (1:1). Yield 56%.

¹H NMR (300 MHz, Chloroform-d) δ 8.96 (s, 1H), 8.81 (s, 1H), 8.54 (d, J = 1.6 Hz, 1H), 8.28 (dd, J = 8.6, 1.6 Hz, 1H), 8.10 (d, J = 8.6 Hz, 2H), 4.03 (s, 6H). m/z= Theoretical 269.07, found 269.1.



Figure S15: FTIR spectrum of dimethyl 4-cyano-2,6-naphthalendicarboxylate (NDC/CN) in KBr.



Figure S16: ¹H-NMR spectrum of dimethyl 4-cyano-2,6-naphthalendicarboxylate (NDC/CN) in CDCl₃.

1.3 Synthesis of 4-cyano-2,6-naphthalenedicarboxylic acid (NDC-COOH/CN)



In a round-bottom flask of 100 mL, 600 mg of (NDC/CN) (2.23 mmol, 1.0 eq) was dissolved in 25 mL THF. Then, 26 mL of KOH solution (1M) was added dropwise. The reaction mixture was stirred for 3h at room temperature. When the reaction was completed, followed by TLC (Heptane/AcOEt 2:1) THF was removed under low pressure and the aqueous phase was acidified to pH 1 with concentrated HCl. The product was obtained by filtration and recrystallized in AcOH. Yield: 76%.

¹H NMR (300 MHz, DMSO-d⁶) δ 8.99 (s, 1H), 8.70 (s, 1H), 8.55 (d, J = 1.6 Hz, 1H), 8.43 (d, J = 8.5 Hz, 1H), 8.20 (dd, J = 8.5, 1.6 Hz, 1H). m/z= theoretical 241.04, found 241.1



Figure S17: FTIR spectrum of 4-cyano-2,6-naphthalendicarboxylic acid (NDC-COOH/CN) in KBr.



COOH/CN) in DMSO-d6.

1.4 Synthesis of Zr-NDC/CN

In a round-bottom flask 100 mL, 150 mg of $ZrCl_4$ (1.0 eq, 0.664 mmol) was initially dissolved in 28 mL of DMF and 1 mL of acetic acid. This solution was heated to 60°C in an ultrasounds bath. Then, a reactive solution containing 1.0 eq of a mixture of naphthalenedicarboxylate derivatives (0.4 eq of 4-cyano-2,6-Naphthalenedicarboxylic acid and 0.6 eq of 2,6-Naphthalenedicarboxylic acid) was dissolved in 9.8 mL of DMF and 48 μ L of water. The reaction mixture was additionally heated to 60°C for 30 min in an ultrasounds bath. Finally, the reaction mixture was heated to 120°C without stirring during 24 h. The reaction mixture was allowed to cool down to room temperature, followed by rising with THF (twice over two days) and diethyl ether (once over one day) finally, the solid was filtrated off and dried in vacuum. Yield 92-95%.



Figure S19: FTIR spectrum of Zr-NDC/CN in KBr.



Figure S20: PXRD of Zr-NDC/CN



Figure S21: TGA pattern of Zr-NDC/CN.



Figure S22: The N2 isotherms (77K) of Zr-NDC/CN.



Figure S23: SEM image of Zr-NDC/CN

1.5 Synthesis of Zr-NDC/Tz

In a round-bottom flask of 10 mL, 200 mg (0.5 mmol-CN, 1 eq) of Zr-NDC/CN and 54.3 mg of NaN₃ (0.83 mmol, 1.5 eq) were suspended-dissolved in 15 mL of anhydrous DMPU. To prevent side-reactions, the organic mixture was bubbled with argon gas and 30.7 mg of $(NH_4)_2Ce(NO_3)_6$ (0.05 mmol, 0.01 eq) was added and heated at 110°C during 24 h. Then an additional portion of NaN₃ and $(NH_4)_2Ce(NO_3)_6$ and was maintained heating for others 24 h. The solid was filtered and washed successively with DMF, water, methanol, ethyl ether and dried under reduced pressure.



Figure S24: FTIR spectrum of Zr-NDC/Tz in KBr



Figure S25: TGA pattern of Zr-NDC/Tz.



Figure S26: SEM image of Zr-NDC/Tz.

1.6 Samples Preparation

For the spectroscopic measurements, the samples were prepared by adding 2 mg of the MOF to 20 mL of acetonitrile (ACN) and sonicating the suspensions for 10 minutes before use. For the experiments in presence of explosive-like molecules, different amounts (expressed in ppm) of the nitroaromatic derivative molecules dissolved in ACN were added to those MOF suspensions and stirred for 5 minutes. To explore the possibility of using these MOFs in more than one sensing experiment, we used the following procedure: (1) 5 mg of the MOF suspensions were suspended in 50 mL of ACN followed by 10 minutes of sonication. (2) We added an amount of TNP in ACN and stirred for 5 minutes. (3) After recording the emission of the MOF without and with TNP, the sample was washed three times with ACN, and the MOF crystals were dried under vacuum. (4) The recovered solid MOF was weighed and an aliquot of TNP in ACN was added to maintain both MOF and TNP concentrations constant. (5) Finally, we recorded again the emission spectrum to get the change in its intensity. This is one of the 6 cycles which we performed.

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