Supplementary Information

Following the light: 3D-printed COF-poly(2-hydroxyethyl methacrylate) dual emissive composite with response to polarity and acidity

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- Section S1. Experimental Section

- Materials

All commercially available reagents were used as received. Water and THF employed to perform the spectroscopic and microscopy analysis of the exfoliated colloids were Milli-Q[®] and spectroscopic grade, respectively and HCl was Suprapur[®] grade from Supelco. Drying of solvents employed in the chemical synthesis of COF precursors was performed by usual methods.

- Methods

(¹³C CP/MAS NMR) spectra were recorded on a Bruker AVANCE III HD-WB 400 MHz with a rotation frequency of 12 kHz.

Fourier transformed infrared (FT-IR) spectroscopy was performed on a PerkinElmer 100 spectrophotometer equipped with a PIKE Technologies MIRacle Single Reflection Horizontal ATR Accessory and on a Bruker TENSOR 27 on a diamond plate.

Mass Spectrometry Bruker Model HCT Ultra Ion Trap Mass Spectrometer (Mass range: 50-6000 amu) (Coupled to HPLC with ESI, APCI and NS interfaces)

Powder x-ray diffraction (PXRD) measurements were carried out with X'PERT MPD with conventional Bragg-Brentano geometry using monochromatic Cu K α 1 radiation (λ = 1.5406 Å) in the 2 θ = 2° - 40° range.

 N_2 sorption isotherms. N_2 (77 K) adsorption-desorption measurements were carried out on a Micromeritics Tristar 3000. Samples were previously activated for 4 h under high vacuum (<10⁻⁷ bar) at 120 °C.

Termogravimetric (TGA) measurements were recorded on a Thermobalance TGA 500 (TA Instruments) with a heating ramp from 20 °C to 830 °C at 10 °C min⁻¹, under N₂ atmosphere.

Differential Scanning Calorimetry (DSC) analyses were performed on a Discovery DSC calorimeter (TA Instruments) with a heating ramp from 20 °C to 200 °C at 10 °C min⁻¹, under N_2 atmosphere.

UV-vis absorption spectra were recorded on an Agilent 8453 spectrophotometer and on a Cary 50 Scan UV-VIS spectrophotometer

Emission spectra were acquired on a Cary Eclipse Fluorescence Spectrometer (Agilent) equipped with a sample holder for solids, a Micro-Raman WITec 300RA using a Nd-YAG 532 nm laser as excitation light source and on a Jasco FP-6300 Spectrofluorometer.

Scanning Electron Microscopy (SEM) images were acquired on a FEI VERIOS 460L microscope.

Transmission electron microscopy (TEM) micrographs were recorded in a JEOL JEM 1400 TEM at 60 kV.

Atomic Force Microscopy (AFM) measurements were performed on a Nanotec Electronica system in dynamic mode, employing commercial Olympus Si/N cantilevers with a nominal force constant of 0.75 N/m and 2 N/m, respectively and SiO₂ (300 nm thickness)/Si surfaces (IMS Company). Prior to their use, the SiO₂ surfaces were sonicated for 15 min in acetone and 15 min

in isopropanol and then dried under an Argon flow. The images were processed using the free downloadable software WSxM (<u>www.nanotec.es</u>).

Synthesis of the COF precursor TAPB¹



- TNPB (1,3,5-Tris(4-nitrophenyl)benzene)

4-nitroacetophenone (1) (23 g, 140mmol) is refluxed in toluene under TfOH (0.5 mL) catalysis for 48h, yields TNPB. After cooling to room temperature, the slurry was filtered giving a black solid which is washed with boiling DMF till the solid turns grey. This product is insoluble in any common deuterated solvent. FTIR (ATR) (cm⁻¹): 1596, 1507, 1344, 1249, 1105, 863, 840, 814, 748, 689. Melting point >300 °C.

- TAPB (1,3,5-Tris(4-aminophenyl)benzene)

TNPB (5 g, 11.3 mmol) and 10% wt Pd/C (0.87 g) were suspended in ethanol (200 mL) under argon atmosphere. The suspension was heated to reflux to obtain a grey solution, then 50-60% v/v hydrazine hydrate (43 mL, 0.5 mol) was added dropwise. The mixture was refluxed overnight, hot filtered over 1 cm Celite pad and cooled to room temperature and then cooled in a fridge. The resulting material was filtered under vacuum and washed with cold ethanol to afford 3.3 g (83%) of **TAPB** as yellow solid. ¹H NMR (300MHz, DMSO-d₆) δ (ppm): 7.53 – 7.43 (m, 9H, Ph), 6.66 (d, J = 8.5 Hz, 6H, Ph), 5.21 (s, 6H, -NH₂). ¹³C-NMR (75MHz, DMSO-d₆) δ (ppm): 145.88, 141.99, 131.93, 128.23, 122.93, 115.39. FTIR (ATR) (cm⁻¹): 3434, 3343, 3221, 3029, 1612, 1511, 1450, 1404, 1280, 1177, 825, 559. MS (ESI): Found C₂₁H₁₈N₆ [M]⁺ 352.1 m/z; Calcd C₂₁H₁₈N₆ [M]⁺ 351.17 m/z. Melting point > 261- 262 °C.

Synthesis of the COF precursors BPTA² and DMTA



- 1,4-dibromo-2,5-dimethoxybenzene (2)

To a solution of 1,4-dimethoxybenzene (1) (5.0 g, 36.2 mmol) in anhydrous CH_2CI_2 (25 mL) Br_2 (9.2 mL, 178 mmol) was added dropwise at room temperature in the absence of light, stirred for 1 h and poured into 1 M KOH. The solution was extracted with CH_2CI_2 , washed with water, dried over MgSO₄, and the solvent was vacuum evaporated. Successive recrystallizations in ethanol yields 1,4-dibromo-2,5-dimethoxybenzene as a white solid (9.65 g, 90%). ¹H NMR (300MHz,

CDCl₃) δ (ppm): 7.10 (s, 2H), 3.85 (s, 6H). ¹³C NMR (75MHz, CDCl₃) δ (ppm): 150.5, 117.1, 110.5, 57.0. FTIR (ATR) (cm⁻¹): 1488, 1431, 1353, 1272, 1207, 1182, 1060, 1015, 855, 754.

- DMTA (2,5-dimethoxybenzene-1,4-dicarbalaldehyde)

A solution of 1,4-dibromo-2,5-dimethoxybenzene (2) (500 mg, 1.67 mmol) in anhydrous THF (8.5 mL) was cooled to -78 °C and *n*-BuLi (1.6 M in hexane, 2.3 mL, 3.68 mmol) was added dropwise. *N*,*N*'-Dimethylformamide (0.6 mL) was added after 3h and the mixture stirred at -78 °C (1 h), warmed to room temperature and stirred one hour. The reaction was quenched with saturated ammonium chloride, THF was eliminated under reduced pressure and the resulting solution extracted with CH₂Cl₂. The organic phase was dried over MgSO₄ and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel flash, 9:1 Hex/EtOAc) to afford **DMTA** as a yellow solid (258 mg, 78 %). ¹H NMR (300MHz, CDCl₃) δ (ppm): 10.49 (s, 2H), 7.45 (s, 2H), 3.94 (s, 6H). ¹³C NMR (75MHz, CDCl₃) δ (ppm): 189.3, 155.7, 129.1, 110.9, 56.2. FTIR (ATR) (cm⁻¹): 2872, 1680, 1478, 1401, 1301, 1214, 1130, 1028, 880, 659. MS (ESI): Found C₁₀H₁₀O₄ [M]⁺ 194.05 m/z; Calcd C₁₀H₁₀O₄₆ [M]⁺ 194.05 m/z.

- DHTA (2,5-dihydroxy-1,4-dicarbalaldehyde)

To a solution of **DMTA** (900 mg, 4.64 mmol) in anhydrous CH_2Cl_2 (20 mL) under Ar atmosphere BBr₃ (1M in CH_2Cl_2 , 20 mL, 20 mmol) was added dropwise at -78 °C. The solution was warmed to RT and stirred overnight. The reaction was quenched with water (40 mL) was added and the resulting mixture was extracted with CH_2Cl_2 . The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure. Finally, consecutive recrystallizations from EtOAc yields 696 mg (90 %) of DHTA. ¹H NMR (300MHz, CDCl₃) δ (ppm): 10.23 (s, 2H), 9.96 (s, 2H), 7.24 (s, 2H). ¹³C NMR (75MHz, DMSO-d₆) δ (ppm): 190.2, 152.8, 127.7, 115.17. FTIR (ATR) (cm⁻¹): 3280, 2888, 1668, 1477, 1281, 1127, 888, 832, 796, 679.

- BPTA (2,5-bis(propargyloxy)-1,4-dicarbaldehyde)

A mixture of **DHTA** (300 mg, 1.8 mmol) and K₂CO₃ (750 mg, 5.44 mmol) in anhydrous DMF (7 mL) was heated at 60 °C for 30 min. Propargyl bromide (80 % wt in toluene, 0.43 mL, 4.0 mmol) was added and the reaction was stirred overnight. Water was added to precipitate the product, which was collected by centrifugation (5 minutes, 6000 rpm). The supernatant was removed, water (10 mL) was added and the mixture centrifuged. This process was repeated 3 times affording a yellow solid which was filtered, dissolved in CH₂Cl₂, dried over MgSO₄ and the solvent removed under reduced pressure. **BPTA** was obtained as a yellow solid (406 mg, 93 %). ¹H NMR (300MHz, CDCl₃) δ (ppm): 10.50 (s, 2H,), 7.60 (s, 2H), 4.86 (d, 4J = 3 Hz, 4H), 2.57 (t, 4J = 3 Hz, 2H). ¹³C NMR (75MHz, CDCl₃) δ (ppm): 188.8, 153.8, 130.1, 113.3, 77.2, 76.9, 57.1. FTIR (ATR) (cm⁻¹): 3278, 3228, 2923, 2874, 2854, 2121, 1679, 1481, 1450, 1421, 1377, 1294, 1205, 1017, 878, 708, 654.

Synthesis of NR-N₃ (2-(2-Azidoethoxy)-9-diethylamino-benzo[a]phenoxazin-5-one)



- 5-(diethylamino)-2-nitrosophenol (5)

Sodium nitrite (69 g, 20 mmol) in water (10 mL) was added over a period of 90 min to a solution of *N-N'*-Diethyl-3-aminophenol (4) (3.3 g, 19.97 mmol) in HCl (7 mL, 36% v/v) and water (4 mL) at 0 °C. The mixture was vigorous stirred for 3.5 h at 0 °C. The resulting solid was filtered and washed with HCl (6 mL, 4M) stirring with a glass stick. The filtrate was dried under vacuum and was used in the next step without further purification.

- NR-OH (2-Hidroxyl-9-diethylamino-5H-benzo[a]phenoxazin-5-one)³

1,6-Dihydroxynaphthol (6) (0.73 g, 4.53 mmol) and 5-(diethylamino)-2-nitrosophenol (5) (1 g, 4.59 mmol) were added to a round bottom flask and dissolved in DMF (100 mL) and refluxed for 4 h. The solvent was vacuum evaporated, and the residue was purified by flash chromatography with 90% EtOAc/iPrOH (1/1) eluant to afford **NR-OH** as a red solid (0.49 g, 32%). ¹H NMR (300MHz, DMSO-d₆) δ (ppm): 10.45 (s, 1H), 7.89 (d, J=2.4 Hz, 1H), 7.59 (d, J=9,1 Hz, 1H), 7.11 (m, 1H), 6.81 (dd, J=9.2; 2.7 Hz, 1H), 6.65 (d, J=2,6 Hz, 1H), 6.16 (s, 1H),3.54 – 3.47 (m, 4H), 1.16 (d, J=6.9 Hz, 6H). ¹³C NMR (75MHz, DMSO-d₆) δ (ppm): 82.5, 161.5, 152.5, 151.6, 147.3, 139.6, 134.6, 131.7, 128.3, 124.8, 119.3, 110.8, 109.0, 105.0, 97.0, 45.3, 13.3.

- NR-Br (2-(2-Bromoethoxy)-9-diethylamino-5H-benzo[a]phenoxazin-5-one)

In a typical synthesis, **NR-OH** (197 mg, 0.60 mmol), K_2CO_3 (496 mg, 3.55 mmol) and 1,2-Dibromoethane (1.54 mL, 17.87 mmol) were dissolved in 2.7 mL of DMF under nitrogen atmosphere and stirred overnight at 65 °C. The solution was concentrated under reduced pressure at 60°C and extracted with CH_2Cl_2 . The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure. The crude material was then purified by flash column chromatography eluting with CH_2Cl_2 and $CHCl_3$ to afford 72 mg (29 % yield) of **NR-Br** as a dark purple solid. ¹H NMR (300MHz, CDCl₃) δ (ppm): 8,24 (d, J=8,7 Hz, 1H), 8,07 (d, J=2,5 Hz, 1H), 7,61 (d, J=9,1 Hz, 1H), 7,21 (dd, J=8,7, 2,6 Hz, 1H), 6,69 (dd, J=9,1, 2,5 Hz, 1H), 6,48 (d, J=2,5 Hz, 1H), 6,34 (s, 1H) 4,37 (t, J= 5,0 Hz, 2H), 3,70 (t, J=4,9 Hz, 2H), 3,48 (q, J=7,1 Hz, 4H), 1,26 (t, J=7,0 Hz, 6H). ¹³C NMR (75MHz, CDCl₃) δ (ppm): 174,61, 160,80, 152,09, 150,80, 146,89, 134,11, 131,11, 127,98, 124,76, 118,44, 109,65, 106,66, 105,48, 101,06, 96,49, 67,43, 50,41, 45,32, 12,93.

- NR-N₃ (2-(2-Azido-ethoxy)-9-diethylamino-benzo[a]phenoxazin-5-one)

NR-Br (90 mg, 0.2 mmol) and NaN₃ (65 mg, 0.38 mmol) were dissolved in anhydrous DMF (2mL) and heated at 80 °C under Argon atmosphere. After 24 h, ice was added to quench the reaction and the resulting suspension was filtrated al washed with water. Finally, after extraction with CHCl₃ and drying with MgSO₄ yields 164 mg (83% yield) of **NR-N₃** as a dark purple solid. ¹H NMR (300MHz, CDCl₃) δ (ppm): 8.24 (d, 3J = 8.7 Hz, 1H), 8.07 (d, 4J = 2.6 Hz, 1H,), 7.60 (d, 3J = 9.0 Hz, 1H), 7.21 (dd, 3J = 8.7 Hz, 4J = 2.6 Hz, 1H), 6.66 (dd, 3J = 9.0 Hz, 4J = 2.8 Hz, 1H,), 6.46 (d, 4J = 2.8 Hz, 1H), 6.31 (s, 1,), 4.37 (t, 3J = 5.0 Hz, 2H), 3. 70 (t, 3J = 5.0 Hz, 2H), 3.46 (q, 3J = 7.4 Hz, 4H), 1.26 ppm (t, 3 J = 7.4 Hz, 6H). ¹³C NMR (75MHz, CDCl₃) δ (ppm): 174.6, 160.8, 152.0, 150.8, 146.8, 134.1, 131.1, 127.9, 124.7, 118.4, 109.6, 106.6, 105.4, 101.0, 96.4, 67.4, 50.4, 45.3, 12.9. FTIR (ATR) v (cm⁻¹): 2963, 2932, 2850, 2098, 1622, 1592, 1505, 1474, 1392, 1351, 1316, 1265, 1203, 1106, 1070, 824.

Synthesis of Alkyne_{0.17}-COF

DMTA (136.3 mg, 0.7 mmol), **BPTA** (34.6 mg, 0.14 mmol), **TAPB** (198.1 mg, 0.56 mmol) and *o*-DCB/n-butanol (3.8 mL/3.8 mL) were introduced in a Pyrex vessel (internal diameter 29 mm, h = 10 cm). The mixture was sonicated for 5 minutes until a homogenous dispersion is produced

and acetic acid (6 M, 0.76 mL). The tube was degassed via 3 freeze-pump-thaw cycles, flame sealed under vacuum and heated at 120 °C for 3 days. The precipitate was collected by filtration and washed with ethanol (6 times over 36 hours), THF (6 times over 36 hours) and air-dried and vacuum dried at 120 °C overnight affording a yellow powder (162 mg, 95 %). ¹³C NMR (100 MHz, ss-CP/MAS) δ (ppm): 154.5, 149.1, 140.5, 138.3, 128.6, 123.1, 117.9, 110.1, 107.8, 80.2, 72.9, 56.8, 55.0. FTIR (ATR) (cm⁻¹): 2926, 1592, 1504, 1464, 1410, 1290, 1211, 1144, 1042, 879, 823, 693. PXRD 20 (°): 2.94, 4.98, 5.76, 7.56, 9.82, 25.5.

General exfoliation procedure by the ultrasonic assisted method (UAM)

 $NR_{0.17}$ -COF (1 mg) and 5 mL of mixture of solvents were added to a 20 mL vial. The mixture was treated for 5 minutes at room temperature in an Elmasonic P 300 H ultrasonic bath with an ultrasonic power effective of 380 W. The resulting suspension was centrifuged at 5000 rpm for 5 min to eliminate non-exfoliated $NR_{0.17}$ -COF. Finally, the supernatant was collected and transferred to a vial.

General exfoliation procedure by the acid self-exfoliation (ASE)

NR_{0.17}-**COF** (1 mg) and 5 mL of acidulated mixtures of solvents (1.1 μ L of HCl 36% v/v per mL of mixture) were added to a 20 mL vial. The mixture was allowed to evolve without stirring during two minutes and the resulting suspension was centrifuged at 5000 rpm for 5 min to eliminate non-exfoliated **NR**_{0.17}-**COF**. Finally, the supernatant was collected and transferred to a vial.

Procedure to calculate the exfoliation yields in THF/water mixtures

 $NR_{0.17}$ -COF (10 mg) and 50 mL of the corresponding mixture of solvents were added to a round bottom flask. The mixture was exposed to the different exfoliation conditions and the resulting suspension was centrifuged at 5000 rpm for 5 min. The non-exfoliated material was collected, washed with water, ethanol and THF and dried under vacuum at 120 °C overnight. Thus, the exfoliation yields were calculated by mass difference.

Table S1. Average height profiles of $NR_{0.17}$ -CONs measured by AFM and exfoliation yields in THF/H₂O mixtures.

Sample	Method	Mixture (THF/H₂O)	Exfoliation yield (%)	Height average (nm)
1	ASE	3/7	11	13.4
2	UAM	3/7	8	48.4
3	ASE	7/3	15	10.4
4	UAM	7/3	12	25.5
5	ASE	9/1	17	11.4
6	UAM	9/1	13	53.9

Determination of the NR_{0.17}-CONs loading in the polymer composites

In order to determine the amount of $NR_{0.17}$ -CONs loaded in the polymer composites, the nonexfoliated COF separated from the polymerizable colloid containing the COF nanosheets, was submitted to several washing cycles consisting of introducing 10 mL of solvent, mixing with the non-exfoliated COF, centrifuging at 4000 rpm for 5 min and removing the supernatant. This procedure was performed using as solvent THF (x3), water (x2) and again THF (x3). Finally, the COF was dried overnight at 120 °C under vacuum. The recovered COF material was weighed and the yield of exfoliation and hence the loading of COF nanosheets in the composites (0.02 mg per gram), was determined as the difference of weight from the initial amount of COF submitted to exfoliation and the final amount of COF recovered.

Parameter	Value	
Exposure time (s)	15	
Bottom exposure time (s)	60	
Lifting height (mm)	5	
Height layer (mm)	0.05	
Lifting speed (mm/min)	65	
Retraction speed (mm/min)	150	

 Table S2. 3D printing parameters used in this work.

- Section S2. UV-vis absorption properties of NR_{0.17}-COF as synthesised



Figure S1. UV-vis diffuse reflectance spectrum of Alkyne_{0.17}-COF (red), Alkyne_{0.17}-COF (black) and NR-N₃ (blue).

Section S3. Thermogravimetric analysis of NR_{0.17}-COF



Figure S2. TGA and DTG curves of NR_{0.17}-COF.

- Section S4. DFT-based theoretical calculations of the optimized layered structures of TAPB-DMTA-COF and NR_{0.17}-COF.

In a first step, molecular fragments involved in the **TAPB-DMTA-COF** and **NR**_{0.17}-**COF** systems were computed within the framework of the density functional theory (DFT) using the Gaussian16 program⁴ with the exchange-correlation hybrid functional CAM-B3LYP⁵ and the ccpVDZ⁶ basis sets. All geometrical parameters were allowed to vary independently, and the calculated geometries were confirmed as minima by frequency calculations.

In a step forward, we used periodic boundary conditions to perform geometry optimization of a battery of stacked 3D layered **TAPB-DMTA-COF** and **NR**_{0.17}**COF** based on their canonical 2D network from the preliminary optimized building blocks. Once the different models of the periodic system were constructed, they were fully optimized (simultaneous lattice/cell and structure optimizations) with the QUANTUM EXPRESSO plane-wave DFT code.⁷ Within this implementation, the GGA-PBE functional⁸ was used to account for the exchange-correlation (XC) effects, at the same time that we use the Grimme DFT-D3 semi-empirical efficient vdW correction to include dispersion forces and energies in conventional DFT functionals.⁹ Ultra-soft pseudopotentials have been used to model the ion-electron interaction within the H, C, N and $O.^{10,11}$ Brillouin zones have been sampled by means of optimal [2×2×1] and [2×2×8] Monkhorst-Pack grids¹² for the 2D layers and 3D crystals, respectively. One-electron wave-functions are expanded in a basis of plane-waves with a kinetic energy cut-off of 42 and 280 Ry for the kinetic energy and electronic density, respectively. The energy cut-off value has been exhaustively studied to achieve sufficient accuracy to guarantee a full convergence in total energy and electronic density. As mentioned, we have performed simultaneous full lattice/cell and structure

optimizations for the different canonical layered 3D system models. The atomic relaxations were carried out within a conjugate gradient minimization scheme until the maximum force acting on any atom was below 0.02 eV Å⁻¹. Interlayer distances have been fully-relaxed following the aforementioned simultaneous lattice/structure relaxation protocol. The crystal-bulk models have been analysed with several intermediate stacking-fashions between their both eclipsed (AA) and staggered (AB) configurations (See Fig. S38)



Figure S3. Optimized 3D crystal-bulk model for TAPB-DMTA-COF.



Figure S4. Optimized 3D crystal-bulk model for NR_{0.17}-COF.

- Section 5. Exfoliation of NR_{0.17}-COF and optical properties in water

ASE exfoliation was first tested in water acidulated at pH = 3 with HCl and compared with the results obtained by the UAM delamination at neutral pH values. In every case, 1 mg of NR_{0.17}-COF was dispersed in 5 mL of the corresponding solvent medium. In the ASE method the mixture was allowed to evolve without stirring during a few minutes, whereas in the UAM assay the sample was treated in an ultrasonic bath for 5 min. The colloidal nature of the COF suspensions was corroborated by Tyndall effect upon irradiation with a laser beam. Finally, the colloidal solutions were separated from the non-exfoliated solid by centrifugation. AFM inspection of the colloidal suspensions revealed a more homogeneous particle distribution for the ASE CONs with an average height around 4 nm and size between 100–300 nm. The particles presented a characteristic angular shape which was corroborated by TEM microscopy (Figs. S5 and S6). In the case of the UAM exfoliation, particles ranging from micrometre size layers to nanometric angular-shaped, like those present in the ASE sample, were detected. The AFM height profiles were larger in this case with values between 5–60 nm (Figs. S7 and S8). These results indicate that acid-assisted exfoliation was more efficient and gave rise to smaller and thinner particles.



Figure S5. Topographic AFM images of a drop-casted $NR_{0.17}$ -CONs ASE colloid on SiO₂ obtained in water at pH = 3 (left) and their related phase images (middle) and height profiles along the depicted lines (right).



Figure S6. TEM micrographs of a drop-casted $NR_{0.17}$ -CONs ASE colloid obtained by exfoliation in water at pH = 3.



Figure S7. Topographic AFM images of a drop-casted $NR_{0.17}$ -CONs UAM colloid on SiO₂ obtained in water at neutral pH (left) and their related phase images (middle) and height profiles along the depicted lines (right).



Figure S8. TEM micrographs of a drop-casted **NR**_{0.17}**-CONs** UAM colloid obtained by exfoliation in water at neutral pH value.

For both types of exfoliations, however, the yield of particles exfoliated was very low, as it could be observed qualitatively by the transparency and lack of colour of the colloids. In fact, the UV-vis absorption spectra (Figure S9) of the samples showed a weak absorption band and shoulder at 270 nm and 400 nm, respectively, which were more intense in the case of the ASE sample (Figure S9a).



Figure S9. a) UV-vis absorption spectra of the colloids obtained from NR_{0.17}-COF by ASE and UAM exfoliation methods in water. b) The same spectra normalized at 410 nm.

Interestingly, both samples exhibited bright green fluorescence ($\lambda_{max} \approx 510$ nm) when excited at 400 nm which is assigned to the COF framework (Figure S10a). The excitation spectra of both colloids support the hypothesis that the emission is originated from protonation of the system (Figure S10b). Thus, in the case of the ASE CONs at pH = 3, the lowest energy band is narrower with a maximum centred at 400 nm, whereas in the case of the UAM sample obtained at neutral pH values, the band is broader with a maximum at 378 nm and a shoulder at ca. 400 nm. This agrees with the presence of two species at neutral pH values, namely the unprotonated and protonated species, that give rise to the same emission. In fact, although the absorption is weak, normalization of the UV-vis spectra allows the detection of a shoulder below 400 nm for the UAM colloid that is not present in the ASE colloid (Figure S9b) and is compatible with the

absorption of the unprotonated system. These results suggest that upon excitation of the UAM colloid, the imine becomes more basic as reported for other Schiff bases and related systems,¹³ and at less a part of the fraction that was unprotonated in the ground state results protonated according to an excited state proton transfer process (ESPT), giving rise to the emission of the protonated form.



Figure S10. a) Emission spectra (λ_{exc} = 390 nm) of ASE NR_{0.17}-CONs colloid (solid line) and UAM NR_{0.17}-CONs colloid (dashed line). Inset: Samples observed under 366 nm light, showing the Tyndall effect. b) Normalized excitation spectra corresponding to both colloids.

With regard to the Nile Red chromophore, its absorption is practically undetectable in the UV-vis spectra (Figure S9a), which is in agreement with the aggregation *via* π - π interactions between of Nile Red units placed in the pores of adjacent COF layers.¹⁴ On the other hand, very weak emission with maxima at 650 and 745 nm is detected upon excitation at 600 nm, being more intense in the case of the ASE colloid. This emission is assigned to protonated Nile Red moieties, by comparison with the emission reported for Nile Red derivatives in acidic media (Figure S11).¹⁵ The protonated species is expected to present much lower quantum yield of emission that the corresponding unprotonated dye.¹⁶



Figure S11. Emission spectra of the colloids obtained from **NR**_{0.17}**-COF** by ASE and UAM exfoliation methods in water, upon excitation at 600 nm.

- Section S6. Exfoliation of the NR_{0.17}-COF material and optical properties in THF/water mixtures.



Figure S12. NR_{0.17}**-COF** ASE (left) and UAM (right) colloids in THF/water mixtures showing the Tyndall effect upon irradiation with a laser beam.



Figure S13. Topographic AFM images of a drop-casted **NR**_{0.17}-**CONs** ASE colloid (mixture THF/water, 3/7, v/v) on SiO₂ (left) and their related height profiles (right) along the depicted lines.



Figure S14. Topographic AFM image of a drop-casted $NR_{0.17}$ -CONs UAM colloid (mixture THF/water, 3/7, v/v) on SiO₂ (a) and its related phase image (b) and height profile along the depicted line (c).



Figure S15. Topographic AFM images of a drop-casted **NR**_{0.17}-**CONs** UAM colloid (mixture THF/water, 7/3, v/v) on SiO₂ (left) and their related phase image (middle) and height profiles along the depicted lines (right)



Figure S16. Topographic AFM image of a drop-casted $NR_{0.17}$ -CONs UAM colloid (mixture THF/water, 7/3, v/v) on SiO₂ (a) and its related phase image (b) and height profile along the depicted line (c).



Figure S17. Topographic AFM images of a drop-casted **NR**_{0.17}**-CONs** ASEcolloid (mixture THF/water, 9/1, v/v) on SiO₂ (left) and their related phase image (middle) and height profiles along the depicted lines (right).



Figure S18. Topographic AFM image of a drop-casted $NR_{0.17}$ -CONs UAM colloid (mixture THF/water, 9/1, v/v) on SiO₂ (a) and its related phase image (b) and height profile along the depicted line (c).



Figure S19. TEM micrographs of a drop-casted $NR_{0.17}$ -CONs ASE colloid obtained in a mixture THF/water, 3/7, v/v.



Figure S20. TEM micrographs of a drop-casted **NR**_{0.17}**-CONs** ASE colloid obtained in a mixture THF/water, 7/3, v/v.



Figure S21. TEM micrographs of a drop-casted $NR_{0.17}$ -CONs ASE colloid obtained in a mixture THF/water, 9/1, v/v.



Figure S22. NR_{0.17}-COF PXRD after UAM and ASE treatments.



Figure S23. Photographs under visible light of the $NR_{0.17}$ -CONs colloids obtained in THF/water mixtures (3/7, 7/3 and 9/1, v/v) by the ASE and UAM exfoliation methods.



Figure S24. UV-vis absorption spectrum of $NR_{0.17}$ -CONs ASE colloid in a mixture THF/water, 3/7, v/v.



Figure **S25.** UV-vis absorption spectrum of $NR_{0.17}$ -CONs ASE colloid in a mixture THF/water, 7/3, v/v.



Figure **S26.** UV-vis absorption spectrum of $NR_{0.17}$ -CONs UAM colloid in a mixture THF/water, 3/7, v/v.



Figure **S27.** UV-vis absorption spectrum of $NR_{0.17}$ -CONs UAM colloid in a mixture THF/water, 7/3, v/v.



Figure **S28.** UV-vis absorption spectrum of $NR_{0.17}$ -CONs UAM colloid in a mixture THF/water, 9/1, v/v.

- Section S6.1. DFT-based theoretical calculations of the photoabsorption spectra of the representative units of the TAPB-DMTA-COF in the protonated and unprotonated forms.

The photoabsorption excitations of the molecular fragments representative of the **TAPB-DMTA-COF** system have been calculated using time-dependent density functional theory (TDDFT),^{17,18} implemented in GAUSSIAN16.⁴ In order to mimic the conditions of the experiments we have accounted in absorption spectra calculations for the influence of a solvent by the Polarizable Continuum Model (PCM)¹⁹ with an effective dielectric constant of $\mathcal{E} = 30$ (corresponding to a 7:3 THF/H₂O solution).



Figure **S29.** Calculated UV-VIS absorption spectra of the molecular fragments representative of the **TAPB-DMTA-COF** unprotonated (black) and protonated (red) in the imine central groups in a mixture THF/water, 7/3. The related electronic transitions and optimized geometries are also shown.



- Section S7. Preparation of fluorescent polymer-CONs composites

Figure S30. a) Emission spectrum of the NR_{0.17}-CONs@HEMA polymerizable colloid containing 2% v/w HCl (37% aqueous solution), solid line, upon excitation at 390 nm, and corresponding excitation spectrum, dashed line. Inset: Fluorescence emitted by the sample under 360 nm UV light. b) Emission of the colloid upon excitation at 600 nm (solid line) and corresponding excitation spectrum (dashed line).



Figure S31. Phase AFM image (up, left) and topographic AFM image (up, right) of a **NR**_{0.17}-**CONs@HEMA** polymerizable colloid drop-casted on SiO₂ and thoroughly washed with EtOH. Bottom: related height profiles along the depicted lines.



Figure S32. Fragments of films corresponding to **NR**_{0.17}**-CONs@pHEMA** (left) and SEM micrograph showing the thickness of the polymeric films (right).



Figure S33. ATR-FTIR of spectrum of the blank pHEMA film (black line) and NR_{0.17}-CONs@pHEMA film (red line).



Figure S34. TGA and DTG curves of the blank pHEMA film (solid line) and NR_{0.17}-CONs@pHEMA film (dashed line).



Figure S35. DSC (solid line) and TGA (dashed line) curves of pHEMA film (a) and NR_{0.17}-CONs@pHEMA film (b) in the region of loss of water.



Figure S36. Variation of the emission maximum for the 2,5-dimethoxy-1,4-phenylbisimine units
 (a) and Nile Red moieties (b) in NR_{0.17}-CONs@pHEMA films treated with different THF/water mixtures. In both cases, the triangle indicates the value for the non-treated film.



Figure S37. a) Picture of NR_{0.17}-CONs@pHEMA a 3D-printed cube and the corresponding blank control after treating the materials with water at pH =1. b) Same samples under a 366 nm UV light.



Figure S38. Side view of the AA stacking configuration and difference in the stacking energy w.r.t. the most stable AA stacking of different representative stacking configurations for the modelled **TAPB-DMTA-COF** (a) and the **NR**_{0.17}-**COF** (b) systems.

- References

- A. Delapeñaruigómez, D. Rodríguez-San-Miguel, K. C. Stylianou, M. Cavallini, D. Gentili,
 F. Liscio, S. Milita, O. M. Roscioni, M. L. Ruiz-González, C. Carbonell, D. Maspoch, R.
 Mas-Ballesté, J. L. Segura and F. Zamora, *Chem. A Eur. J.*, 2015, **21**, 10666–10670.
- 2 H. Xu, J. Gao and D. Jiang, *Nat. Chem.*, 2015, **7**, 905–912.
- 3 J. Jose and K. Burgess, J. Org. Chem., 2006, **71**, 7835–7839.
- 4 *Gaussian 16, Revision C.01*, M. J. Frisch *et al.*, Gaussian, Inc., Wallinford CT, 2016.
- 5 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51–57.
- 6 T. H. Dunning, J. Chem. Phys., 1989, **90**, 1007–1023.
- P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L.
 Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi *et al.*,
 J. Phys. Condens. Matter, 2009, **21**, 395502.
- 8 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 9 S. Grimme, J. Comput. Chem., 2006, **27**, 1787–1799.
- 10 A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227–1230.
- 11 N. Mounet and N. Marzari, *Phys. Rev. B*, 2005, **71**, 205214.
- 12 J. D. Pack and H. J. Monkhorst, *Phys. Rev. B*, 1977, **16**, 1748–1749.
- 13 W. Sheng, M. Nairat, P. D. Pawlaczyk, E. Mroczka, B. Farris, E. Pines, J. H. Geiger, B. Borhan and M. Dantus, *Angew. Chemie Int. Ed.*, 2018, **57**, 14742–14746.
- 14 A. Ray, S. Das and N. Chattopadhyay, ACS Omega, 2019, 4, 15–24.
- 15 M. Börgardts, K. Verlinden, M. Neidhardt, T. Wöhrle, A. Herbst, S. Laschat, C. Janiak and T. J. J. Müller, *RSC Adv.*, 2016, **6**, 6209–6222.
- 16 N. I. Selivanov, L. G. Samsonova, V. Y. Artyukhov and T. N. Kopylova, *Russ. Phys. J.*, 2011, **54**, 601–606.
- 17 A. Rubio, L. C. Balbás and J. A. Alonso, *Phys. Rev. B*, 1992, **45**, 13657–13663.
- M. E. CASIDA, Time-Dependent Density Functional Response Theory for Molecules.
 1995, World Scientific (Singapore), 1995, pp. 155–192.
- 19 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3093.