Supporting Information for

Donor-Acceptor Organogels and Xerogels from C_3-symmetric Pyrene and Naphthalene-diimide Components

Fanny Peigneguy,[†,a] Cristina Oliveras-González,[†,a] Marie Voltz,[a] Nagham Ibrahim,[a] Marc Sallé,[a,*] Narcis Avarvari[a,*] and David Canevet[a,*]

[a] *Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F-49000 Angers, France. E-mail: marc.salle@univ-angers.fr; narcis.avarvari@univ-angers.fr; david.canevet@univ-angers.fr*

[†] *F.P. and C.O.-G. contributed equally to this work*

➢ Synthetic details

All reagents were purchased from commercial sources and used without further purification unless otherwise stated. The 3,3'-diamino-2,2'-bipyridine was prepared as described in the literature.[S1] Reactions were carried out under argon atmosphere with freshly distilled solvents. Microwave (MW) assisted reactions were performed using a Biotage initiator$^+$ system. Thin-layer chromatography (TLC) was carried out with ALUGRAM aluminum sheets coated on silica gel (SiOH, normal phase, Xtra SIL G UV254, 20 x 20 cm) from MACHEREY-NAGEL. Compounds were detected with UV irradiation (λ = 254 nm and λ = 365 nm) from Bioblock Scientific. Purifications of steps **1** and **2** were performed using column chromatography on silica gel SiO_2 from Sigma Aldrich (technical grade, pore size 60 Å, 230-400 mesh particle size) and analytical standard solvents as eluent. Purification of **C_3NDI** was performed on a LC-9160NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT and RI-700 II detectors at room temperature through a set of two JAIGEL-2H and 2.5H columns at an elution rate of 10 mL/min. ^{1}H and ^{13}C NMR were recorded on a Bruker AVANCE III 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or on Bruker AVANCE DRX 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Chemical shifts (δ) are given in parts-per-million (ppm) relative to TMS and coupling constants (J) are represented in Hertz (Hz). HRMS was achieved on Bruker Biflex III (MALDI-TOF) or Jeol JMS 3000 (SPIRAL-TOF-TOF) mass spectrometers.

➢ Gel formation

Organogels were prepared from individual gelators **C_3Pyr**, **C_3NDI** or their equimolar mixtures **C_3Pyr**/**C_3NDI** in organic solvents. The gelators were weighed in a vial (V = 3 mL) and the desired amount of solvent was added. The corresponding suspensions were sonicated for 5 min before being heated at high temperature. To do so, the vials were placed on a heating plate, whose temperature was set at a temperature T = bp + 30 °C, until complete solubilisation. Then, vials were placed on a bench and allowed to cool down at room temperature until gel formation.

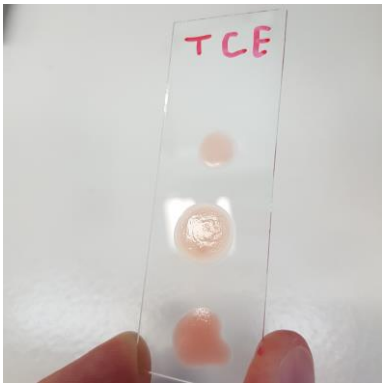
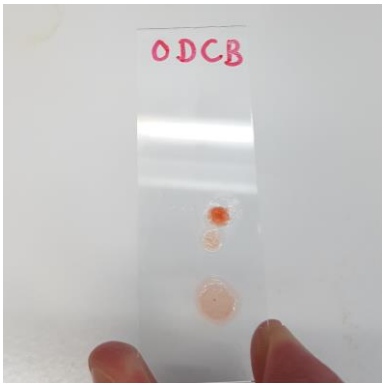
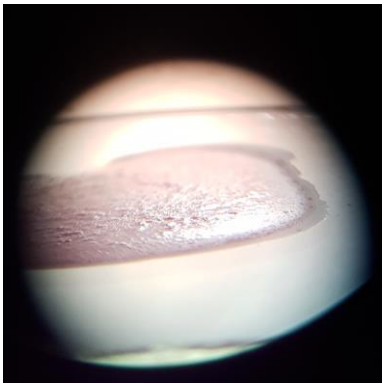
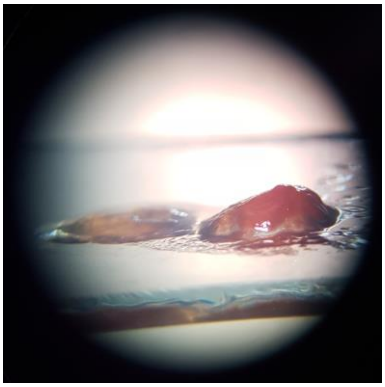
➢ Xerogel preparation

Xerogels were prepared on glass slides by gel deposition or by drop casting hot solutions of individual compounds **C_3Pyr**, **C_3NDI** and their mixtures **C_3Pyr**/**C_3NDI**, and subsequent evaporation of the solvent.

To prepare the samples obtained by **deposition of a piece of gel**, a gel sample was prepared and a piece of gel (about 50 mg) was cautiously deposited on the glass slide. The solvent was subsequently evaporated overnight under a bench.

To obtain the samples through **the drop casting technique**, a gel was first formed in a vial according to the "Gel formation" section. It was subsequently heated until the typical colour for charge transfer complexation disappeared, until the complete solubilisation of solid particles, while maintaining the temperature below the boiling point of the solvent to avoid evaporation and hence, variations of concentration. Once this state reached, the glass slides was heated to avoid an abrupt cooling process that might favour precipitation and limit gelation. A Pasteur pipette was also heated to avoid such a phenomenon. This allowed the deposition of three to five drops of warm solution, which eventually gelled over the glass slide over evaporation (Table S1). This was confirmed by taking pictures of the corresponding organogels prepared from *o*-dichlorobenzene, 1,1,2,2-tetrachloroethane and *N,N*-dimethylformamide.

Table S1. Pictures of gel materials formed by drop casting warm solutions (C = CGC)

TCE	*o*DCB	DMF
		
		

➢ **UV-visible absorption spectroscopy**

UV-visible absorption spectra were recorded on a JASCO V-730 UV-vis spectrophotometer in a quartz cuvette of 1 mm path length. Absorption measurements as a function of temperature were carried out in the range 20 °C - 100 °C.

➢ **Scanning electron microscopy**

Scanning electron microscopy can reproduce the topography of the sample. It uses an electron beam that scans the sample at any point causing the formation of low energy secondary electrons which are then converted into an electrical signal.

Images were recorded using a JEOL JSM6301F microscope. Xerogels were prepared on a glass slide 1cmx1cm by gel deposition or by drop casting hot solution of individual compounds C_3Pyr, C_3NDI and their mixtures C_3Pyr/C_3NDI, then the solvent left to evaporate. Afterwards, xerogel samples were covered with a 5 nm layer of platinum using the LEICA ACE600 metallizer to facilitate MEB measurements.

➢ **Fluorescence spectroscopy**

Fluorescence emission spectra were recorded on a JASCO FP-8500 spectrofluorometer at room temperature in a cuvette of 1 cm path length (for C_3NDI at 10^{-5} M in TCE) or in a quartz NMR tube (for the individual compounds **C_3Pyr**, **C_3NDI** and their equimolar mixture **C_3Pyr/C_3NDI** at critical gelation concentrations of mixed organogels).

➢ **Confocal microscopy**

Images were recorded using a Leica SP8 confocal microscope. Widely used in molecular biology, confocal microscopy allows to obtain images with a shallow depth of field. The light source is a monochromatic laser that scans the sample point by point along the x-axis and y-axis to reproduce a two-dimensional image. Scanning can be performed at different altitudes moving the sample by a dz increment to obtain several planes which will reproduce a three-dimensional image.

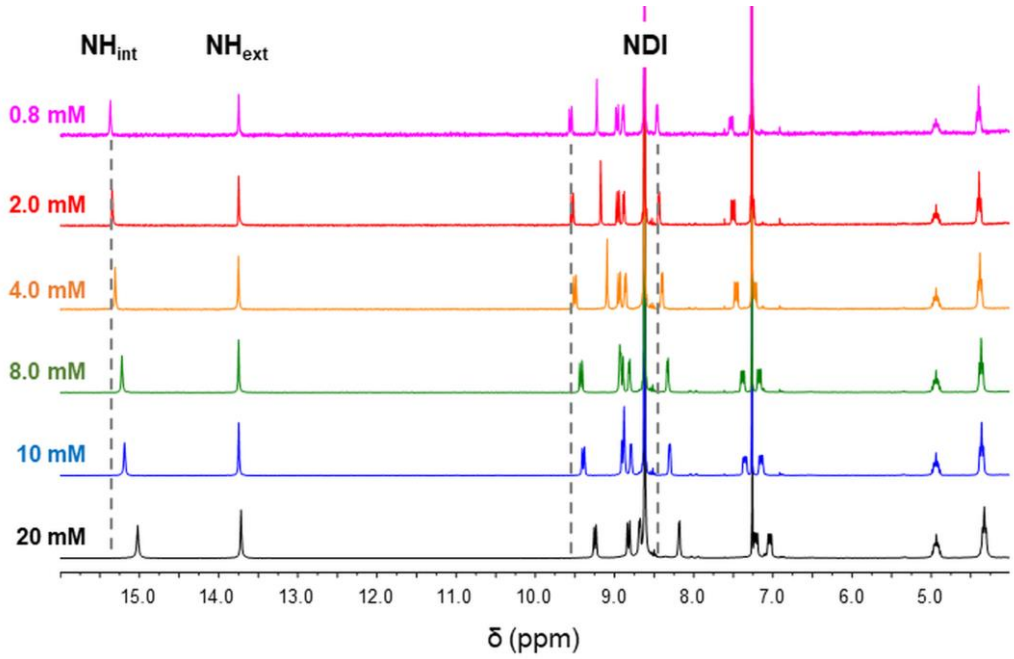


Figure S1. Variable-concentration ^{1}H NMR spectroscopy of **C_3NDI** ($CDCl_3$, 293 K).

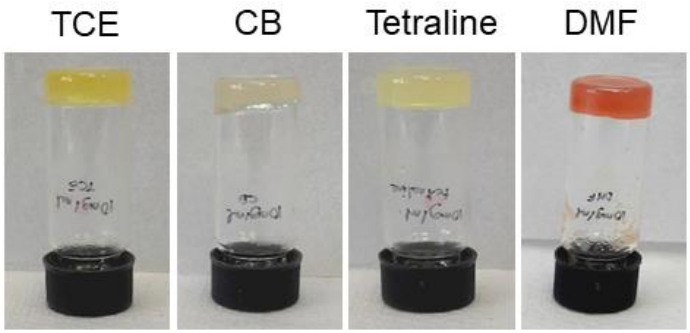


Figure S2. Pictures of gels obtained from **C_3NDI**.

Table S2. Comparison of the gelation properties of **C_3Pyr** and **C_3NDI** in miscellaneous solvents. (I = Insoluble (10 mg.mL^{-1}) ; S = Solution; G= Gel (CGC); C = Colloid). MCH stands for methylcyclohexane.

Solvent	C_3Pyr	C_3NDI	b.p. (°C)	Relative permittivity	Dipolar moment (D)	δ_D (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)
Toluene	I	I	111	2.38	0.38	18.04	2.01	1.39
MCH	I	I	101	2.02	0	16.03	0	0
THF	I	I	66	7.52	1.75	16.83	8.02	5.72
ACN	I	I	82	36.6	3.92	15.33	6.11	18.04
DCM	I	I	40	8.9	1.60	18.25	6.31	6.11
$CHCl_3$	I	S (70)	61	4.8	1.04	17.84	5.72	3.12
TCE	G (65)	G (60)	146	8.5	1.32	18.80	5.30	5.10
CB	G (12)	G (12)	134	5.7	1.69	19.04	2.01	4.31
Tetraline	G (36)	G (1.2)	208	2.8	0	19.64	2.01	2.91
***o*DCB**	G (8)	G (1.2)	179	10.1	2.5	19.25	3.30	6.31
DMSO	I	C	189	47.2	3.96	18.45	16.44	10.26
DMF	I	G (5)	153	38.2	3.82	17.45	13.74	11.32

Figure S3. C_3Pyr/C_3NDI (1:1) organogels obtained in different solvents (TCE, DMF, *o*DCB).

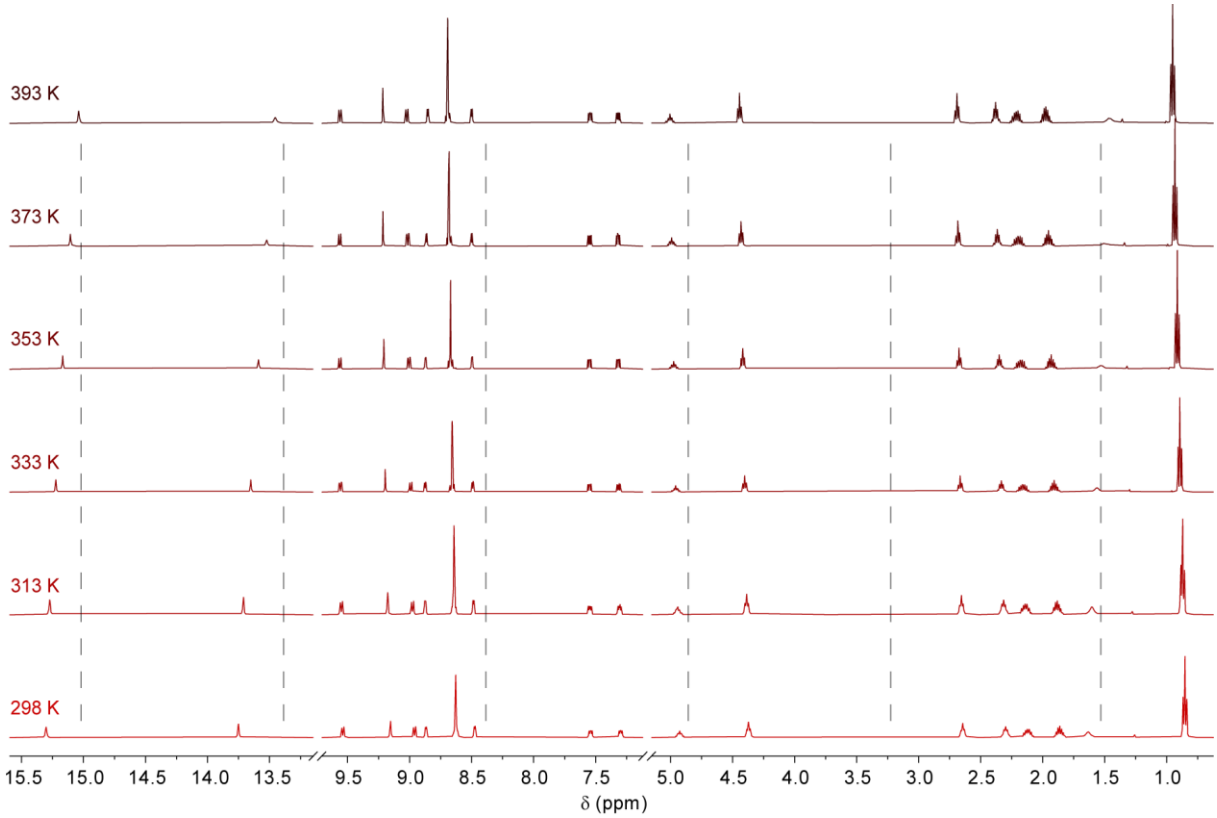


Figure S4. Variable temperature ^{1}H NMR spectroscopy of **C_3NDI** (5.2 mM, TCE-d_2, 500 MHz)

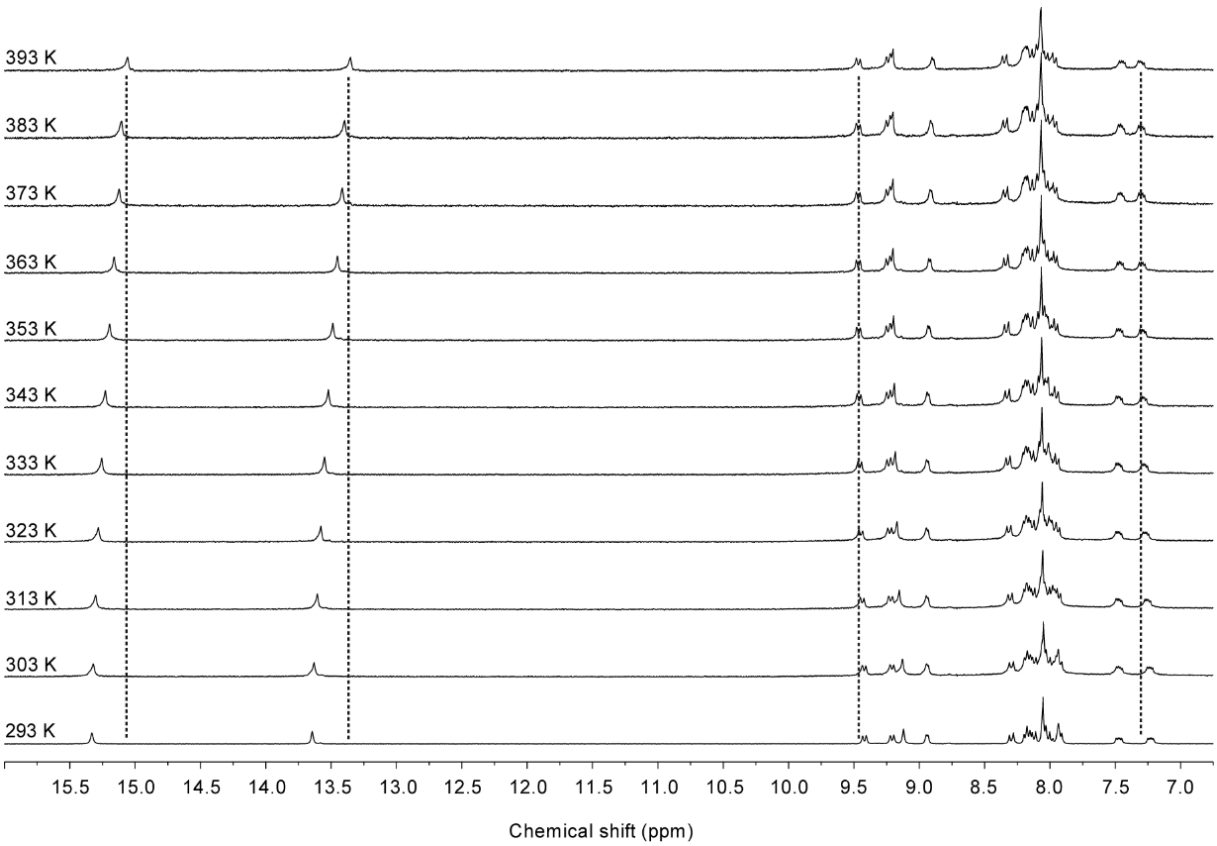


Figure S5. Variable-temperature ^{1}H NMR spectroscopy of **C_3Pyr** (3.3 mM, TCE-d_2, 500 MHz) (reproduced with the permission of Wiley-VCH; order number: 5286530749184).

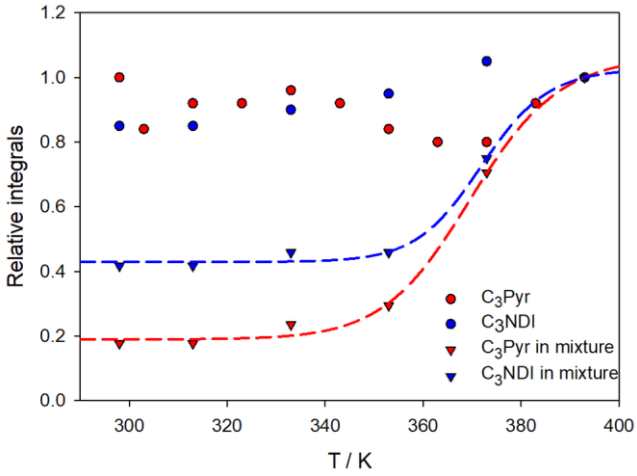


Figure S6. The present figure shows the evolution of the integrals of **C₃Pyr** and **C₃NDI** upon cooling solutions of pure **C₃Pyr** and pure **C₃NDI** (5.2 mM, circles), or a 1:1 mixture of **C₃Pyr** and **C₃NDI** (C_T = 10.4 mM, triangles). The relative integrals were calculated by dividing the integrals at a given temperature by the integral of the same signal at 393 K. Values were respectively calculated from signals located at δ = 9.46 (**C₃Pyr**) and 9.55 ppm (**C₃NDI**) at 393 K).

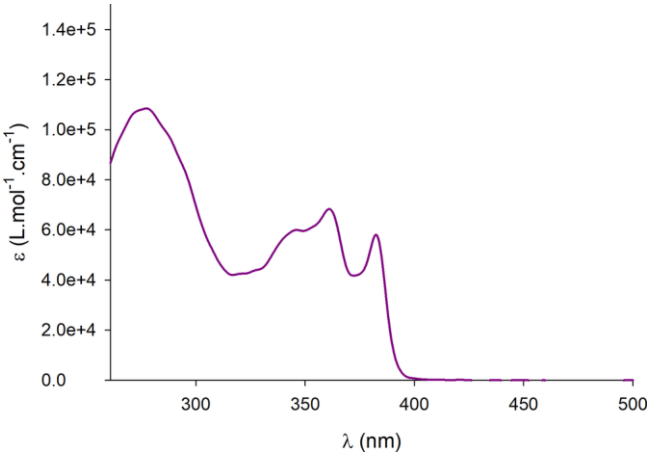


Figure S7. UV-visible absorption spectrum of the individual compound **C₃NDI** (10^{-5} M) in TCE.

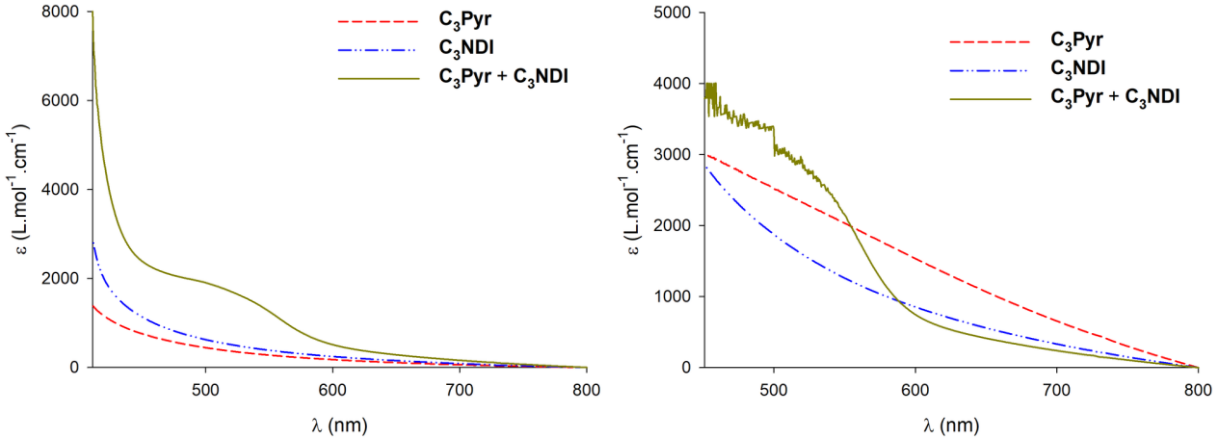


Figure S8. *Left*. UV-visible absorption spectra of **C₃Pyr** (2.3 mM), **C₃NDI** (2.3 mM) and their equimolar mixture (C_T = 4.6 mM) in *o*DCB. *Right*. UV-visible absorption spectra of **C₃Pyr** (4.3 mM), **C₃NDI** (4.3 mM) and their equimolar mixture (C_T = 8.6 mM) in DMF.

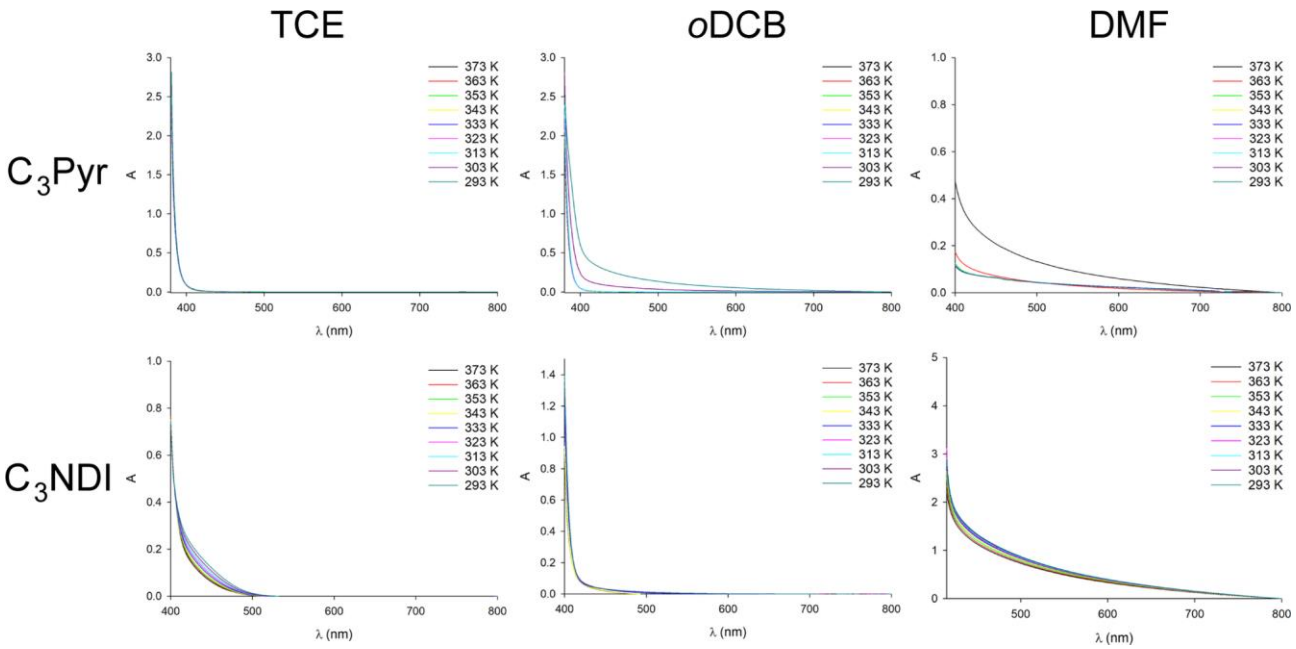


Figure S9. Evolution of the UV-visible absorption spectra of **C_3Pyr** and **C_3NDI** in TCE (C = 5.2 mM), *o*DCB (C = 2.3 mM) and DMF (C = 4.3 mM) upon cooling the samples from 100 to 20°C.

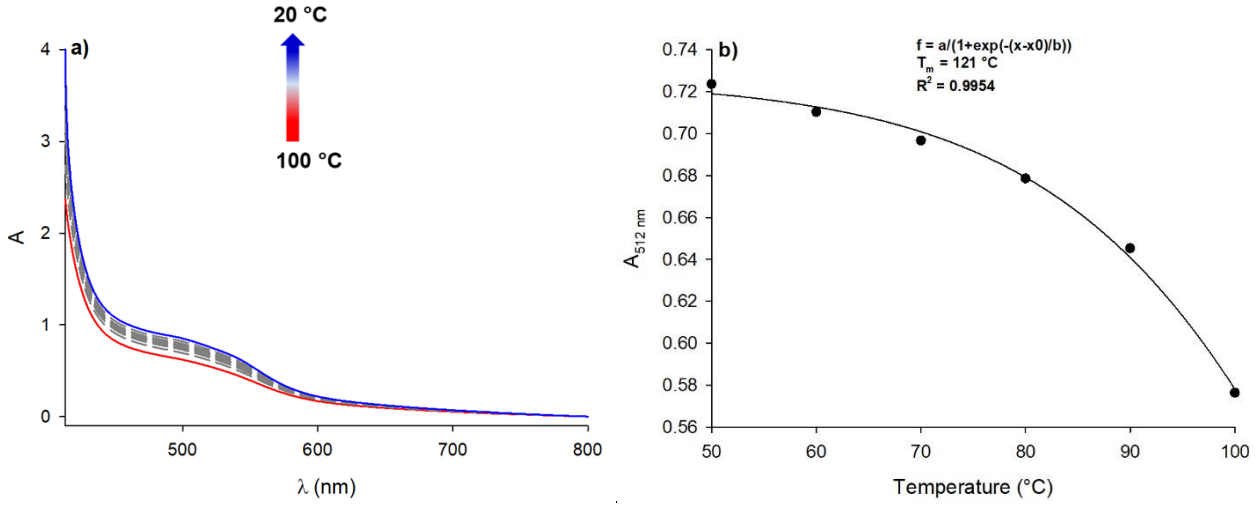


Figure S10. (a) Evolution of the UV-visible absorption spectrum of a **C_3Pyr**/**C_3NDI** (1:1) mixture in *o*DCB ([**C_3Pyr**] = [C_3NDI] = 4.6 mM) upon decreasing the temperature from 100 °C (red curve) to 20 °C (blue curve) (interval of 10 °C between each curve). (b) Corresponding evolution of the absorbance at λ = 512 nm in *o*DCB as a function of temperature.

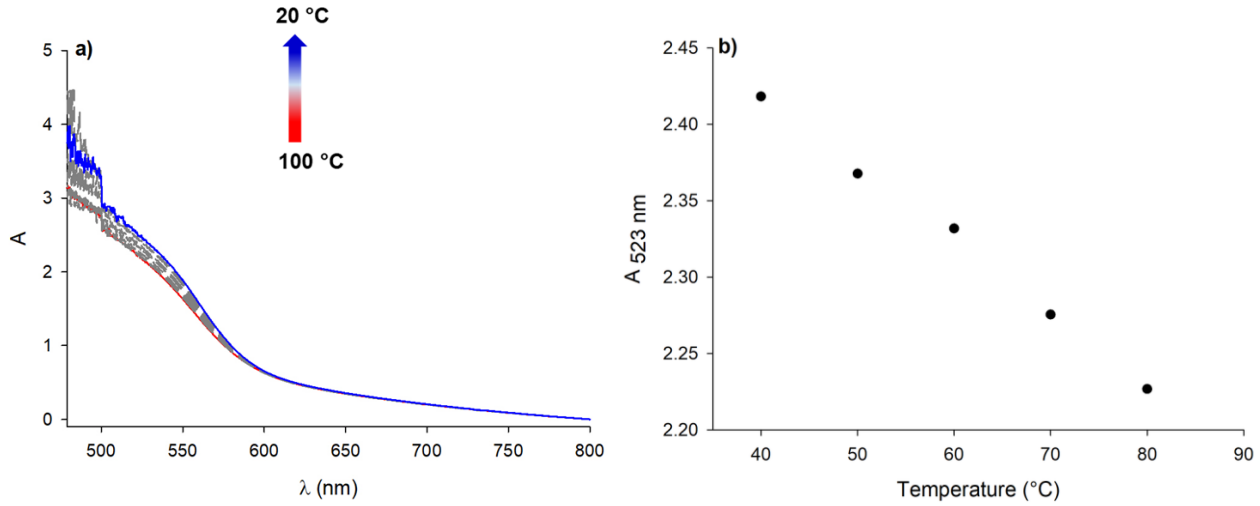


Figure S11. (a) Evolution of the UV-visible absorption spectrum of a **C_3Pyr/C_3NDI** (1:1) mixture in DMF ([**C_3Pyr**] = [**C_3NDI**] = 4.3 mM) upon decreasing the temperature from 100 °C (red curve) to 20 °C (blue curve) (interval of 10 °C between each curve). (b) Corresponding evolution of the absorbance at λ = 523 nm in DMF as a function of temperature.

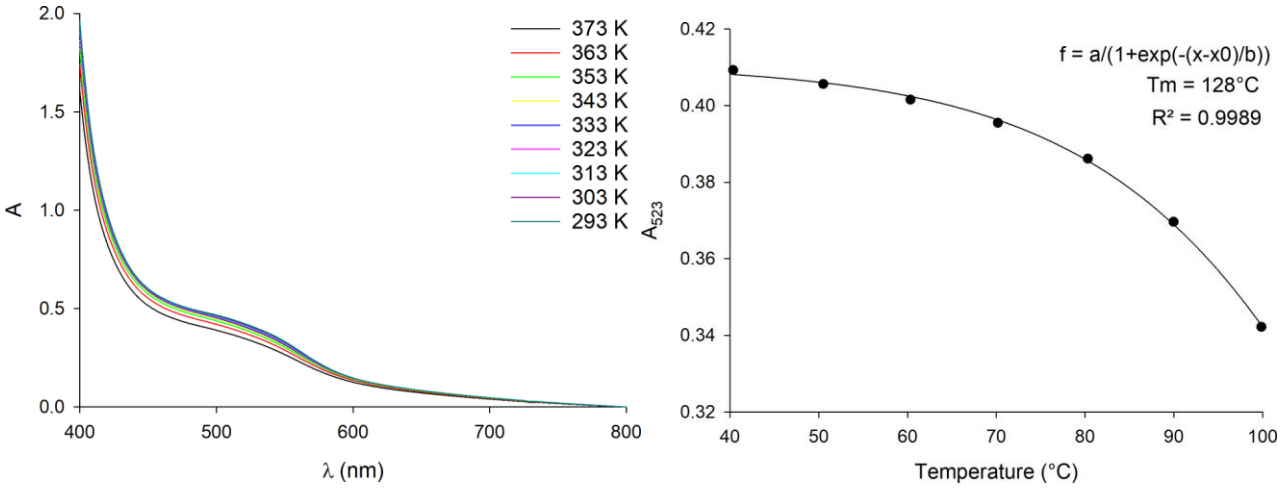
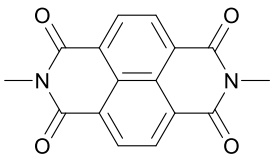


Figure S12. (a) Evolution of the UV-visible absorption spectrum of a C_3Pyr/C_3NDI (1:1) solution in DMF ([**C_3Pyr**] = [**C_3NDI**] = 0.43 mM) upon decreasing the temperature from 100 °C (red curve) to 20 °C (blue curve) (interval of 10 °C between each curve). (b) Corresponding evolution of the absorbance at λ = 523 nm in DMF as a function of temperature.



Scheme S1. Chemical structure of *N,N*-dimethylnaphthalene diimide

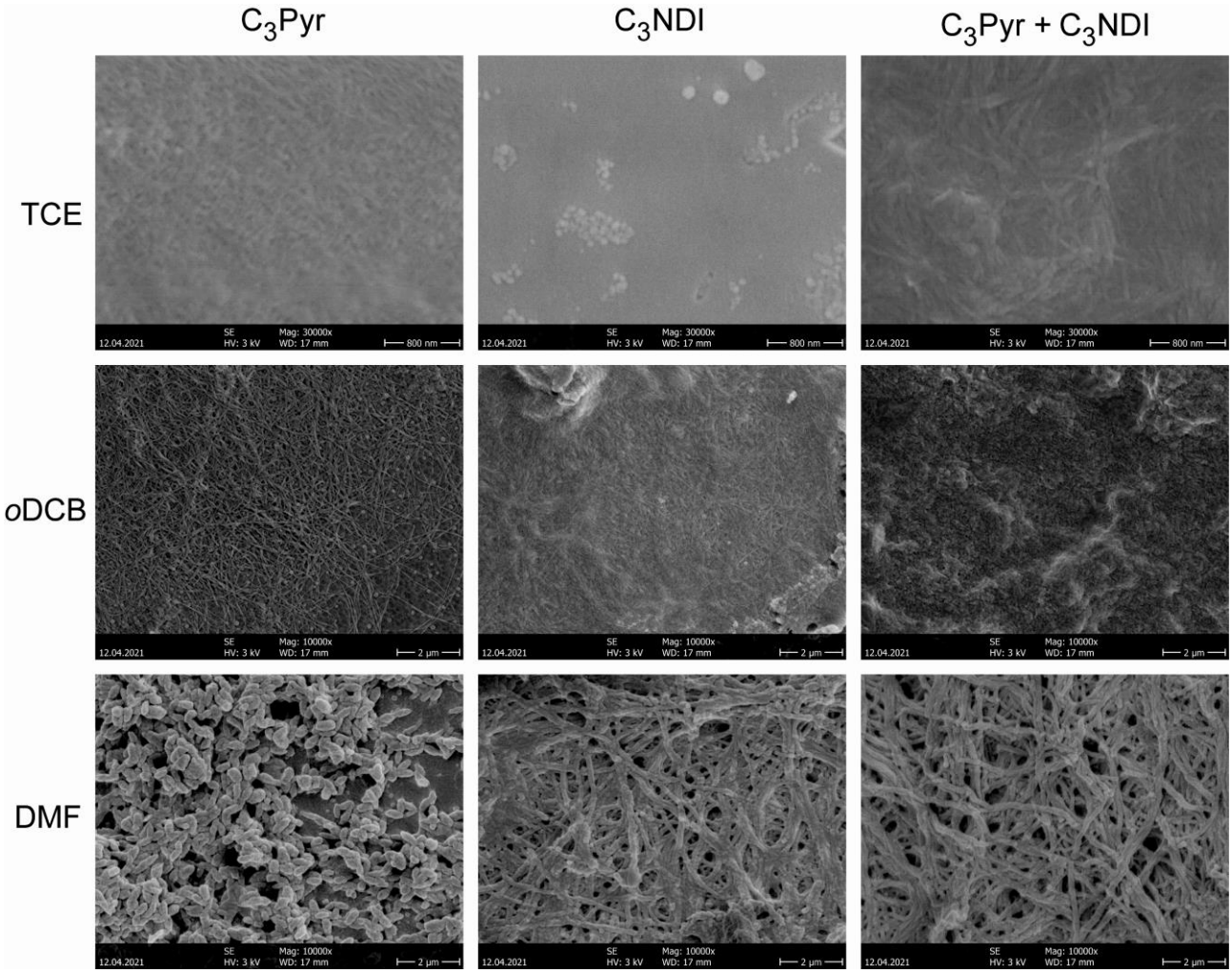


Figure S13. SEM Micrographs of films obtained by drop casting warm solutions of **C_3Pyr**, **C_3NDI** and their equimolar mixtures (C = CGC, except for **C_3Pyr** in DMF, which affords suspensions).

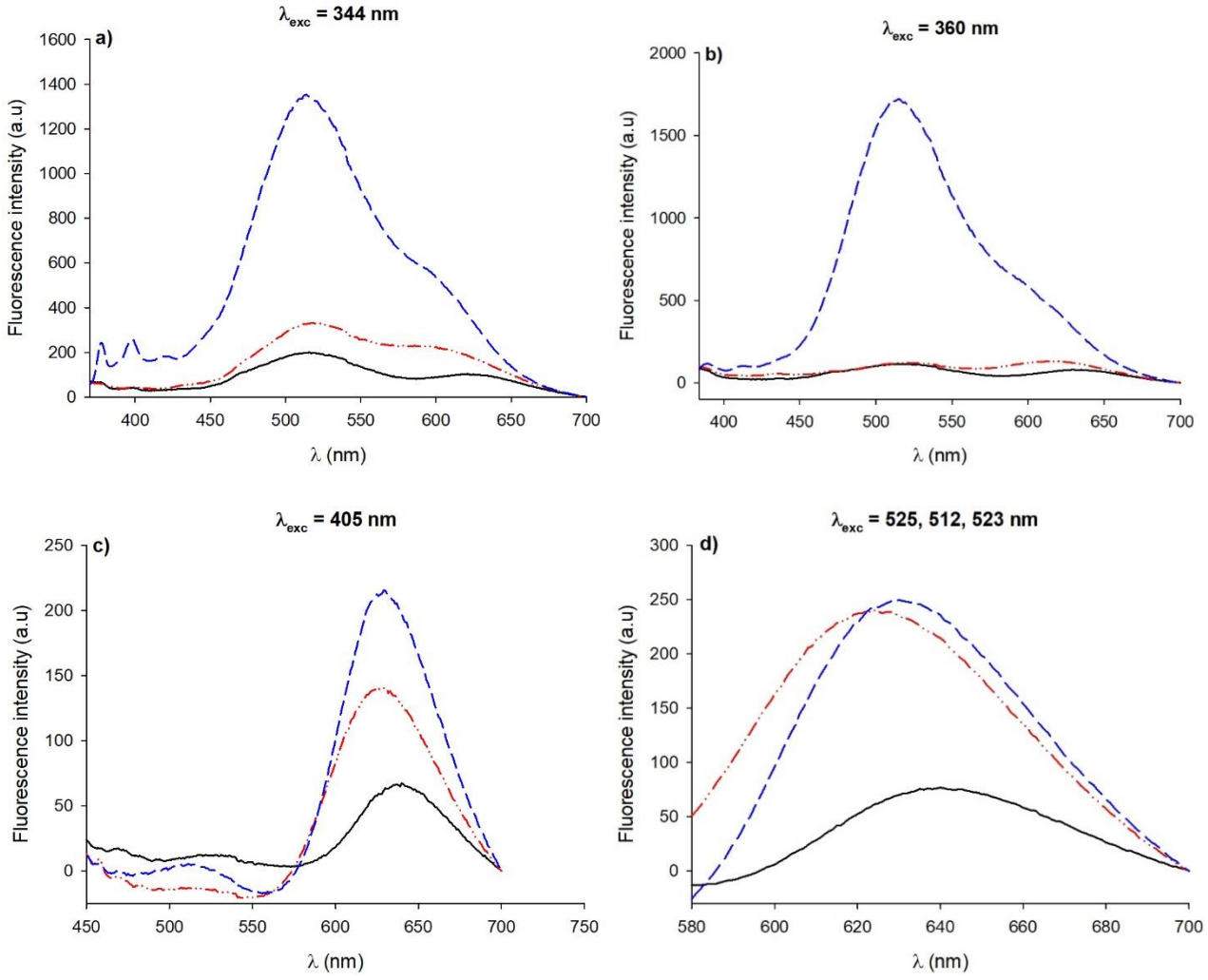


Figure S14. Emission spectra of **C_3Pyr/C_3NDI** (1:1) organogels at critical gelation concentrations in TCE (black solid line), in *o*DCB (red dash-dot-dot), in DMF (blue medium dash) for a) λ_{exc} = 344 nm (pyrene), b) λ_{exc} = 360 nm (NDI), c) λ_{exc} = 405 nm and d) λ_{exc} = 520 nm (charge-transfer complex)

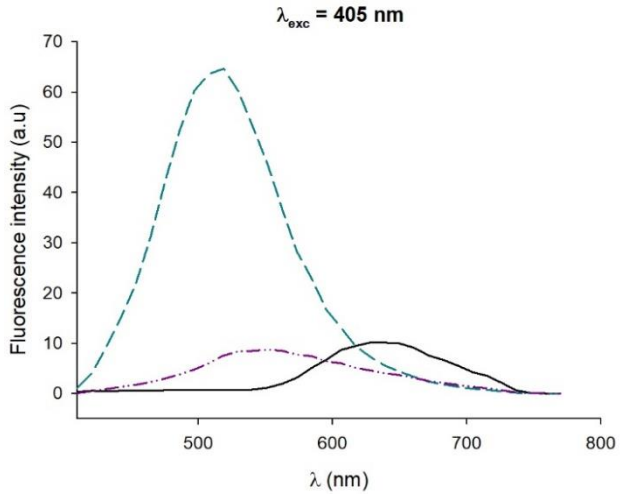


Figure S15. Emission spectra obtained by confocal microscopy of films prepared by deposition of individual compounds **C_3Pyr** (8 mg/mL, dark cyan medium dash), **C_3NDI** (10 mg/mL, dark pink dash-dot-dot) and their equimolar mixture **C_3Pyr/C_3NDI** (identical concentrations, gel state, black solid line) in TCE for λ_{exc} = 405 nm.

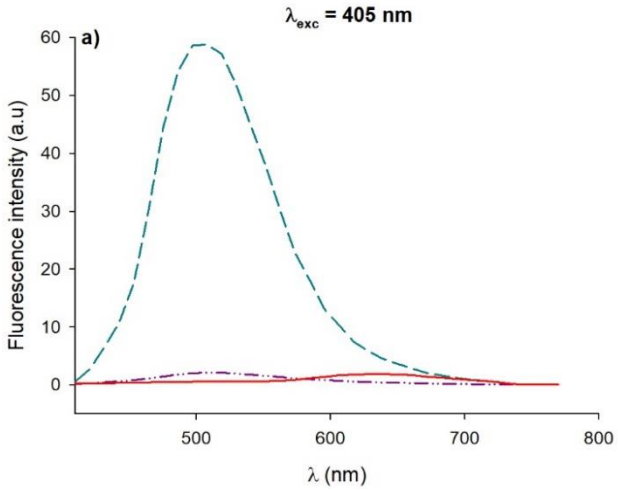


Figure S16. Emission spectra obtained by confocal microscopy of films prepared by deposition of individual compounds **C_3Pyr** (3.5 mg/mL, dark cyan medium dash), **C_3NDI** (4.4 mg/mL, dark pink dash-dot-dot) and their equimolar mixture **C_3Pyr**/**C_3NDI** (identical concentrations, gel state, red solid line) in *o*DCB for λ_{exc} = 405 nm.

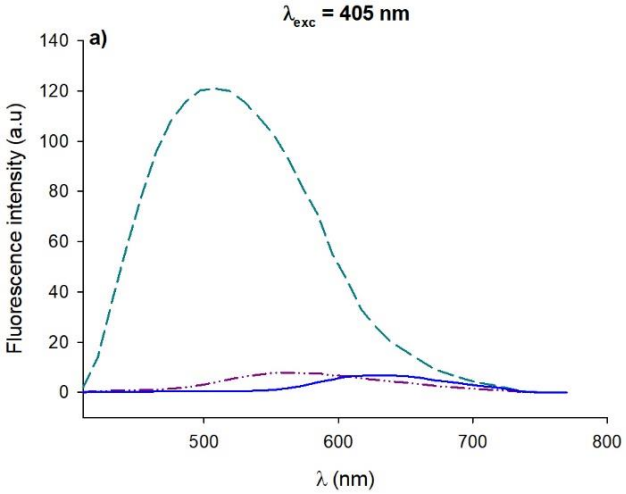


Figure S17. Emission spectra obtained by confocal microscopy of films prepared by deposition of individual compounds **C_3Pyr** (6.5 mg/mL, dark cyan medium dash), **C_3NDI** (8.2 mg/mL, dark pink dash-dot-dot) and their equimolar mixture **C_3Pyr**/**C_3NDI** (identical concentrations, gel state, blue solid line) in DMF for λ_{exc} = 405 nm.

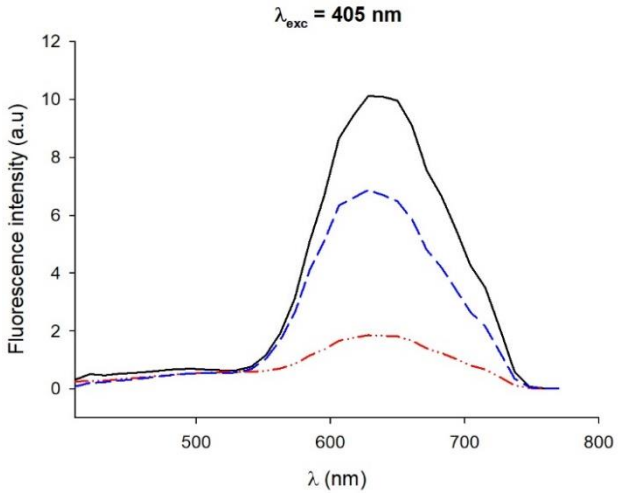
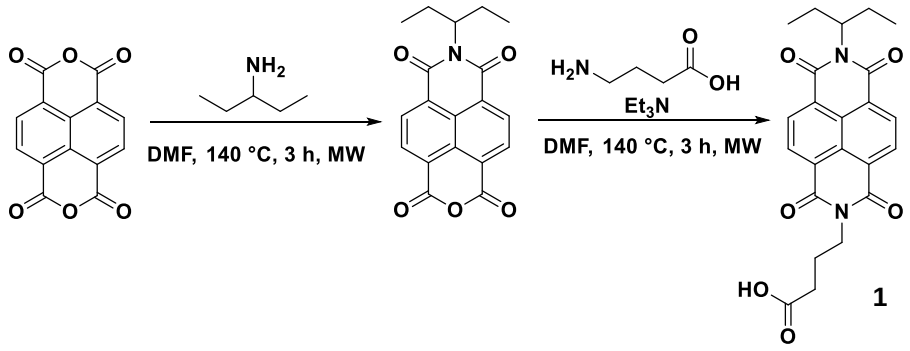


Figure S18. Emission spectra obtained by confocal microscopy of xerogels prepared by gel deposition of **C_3Pyr/C_3NDI** (1:1) mixtures at critical gelation concentrations in TCE (black solid line), *o*DCB (red dash-dot-dot), DMF (blue medium dash) for λ_{exc} = 405 nm.

Compound **1**.



In a microwave tube, 1,4,5,8-naphthalenetetracarboxylic dianhydride (800 mg, 2.98 mmol, 1 eq) was suspended in dry DMF (16 mL) and 3-aminopentane (0.33 mL, 2.83 mmol, 0.95 eq) was added under argon atmosphere. The suspension was allowed to sonicate for 5 min and was heated at 140 °C for 3 h under microwave irradiation. The solvent was evaporated *in vacuo* and the dark-brown solid was solubilized in acetone. Hydrochloric acid (1 M) was then added into the solution until precipitation. The suspension was stirred at room temperature for 10 min and was filtered under vacuum to get back the beige-brown precipitate which was washed with water several times and dried *in vacuo* overnight. The crude (737 mg) was used for the next reaction without any other purification.

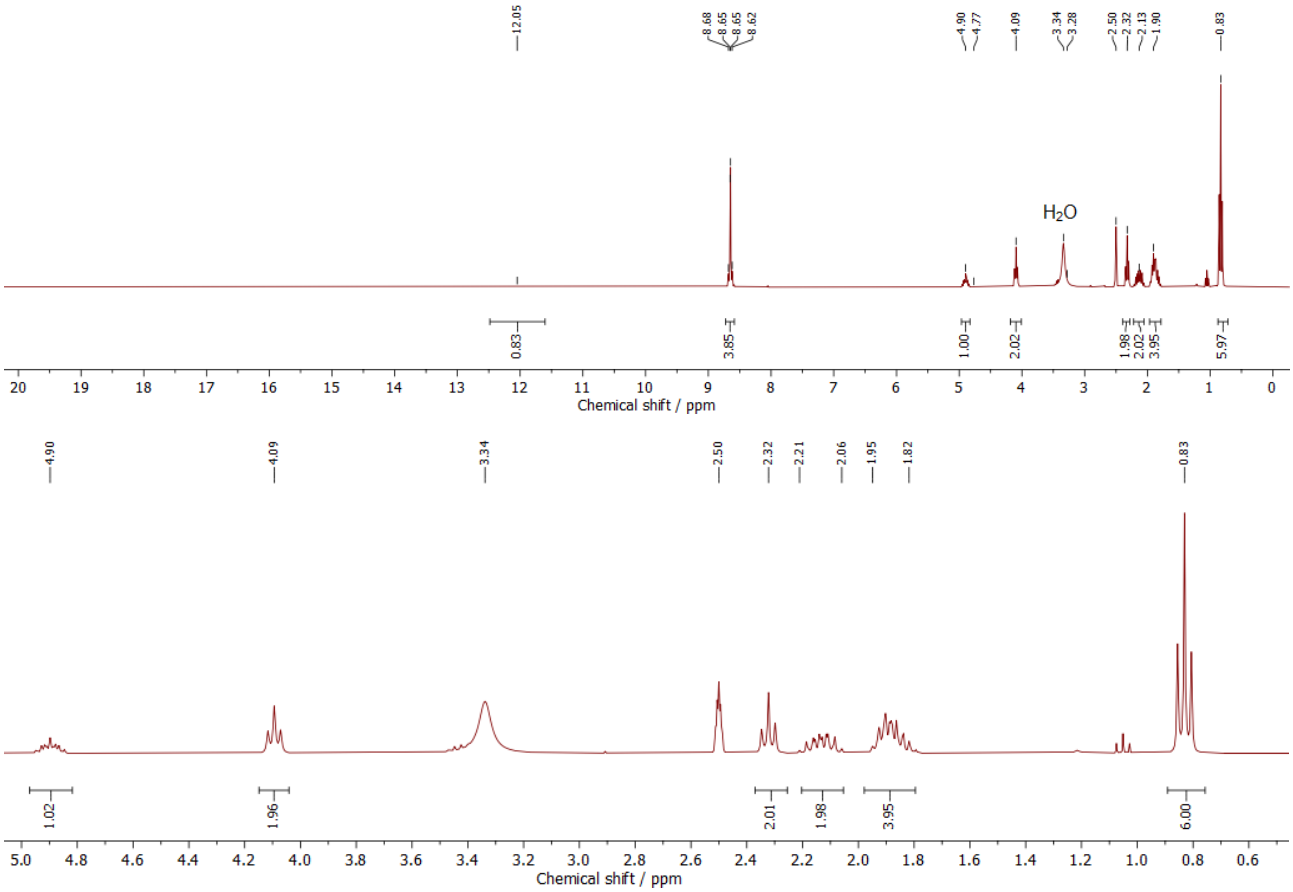
In a microwave tube, the crude (737 mg, 2.2 mmol, 1 eq) and 4-aminobutanoic acid (236 mg, 2.29 mmol, 1.05 eq) were dissolved in dry DMF (17 mL), then triethylamine (0.32 mL, 2.29 mmol, 1.05 eq) was added under argon atmosphere. The suspension was allowed to sonicate for 5 min and was heated at 140 °C for 3 h under microwave irradiation. The solvent was evaporated *in vacuo* and the dark-brown solid was suspended in a mixture of water/methanol (2:1). Few drops of hydrochloric acid (6 M) were then added and the mixture was stirred at room temperature for 10 min. The suspension was filtered and was washed with water several times before being dried *in vacuo* overnight. The beige-brown solid was purified using silica gel chromatography (PE:EtOAc, 8:2 to 5:5) to get a beige-white solid (265 mg, 28 %).

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 12.04 (s, 1H, COO**H**), 8.67 (d, *J* = 7.7, 2H, Ar_{NDI}), 8.63 (d, *J* = 7.6, 2H, Ar_{NDI}), 4.90 (tt, *J* = 9.4, 5.8 Hz, 1H, $CH_{aminopentane}$), 4.09 (t, *J* = 6.8 Hz, 2H, **CH_2**-$N(CO)_2$), 2.32 (t, *J* = 7.3 Hz, 2H, **CH_2**-COOH), 2.21-2.06 (m, 2H, $CH_{2aminopentane}$), 1.95-1.79 (m, 4H, $CH_{2aminopentane}$, $CH_{2central}$), 0.83 (t, *J* = 7.4 Hz, 6H, CH_3).

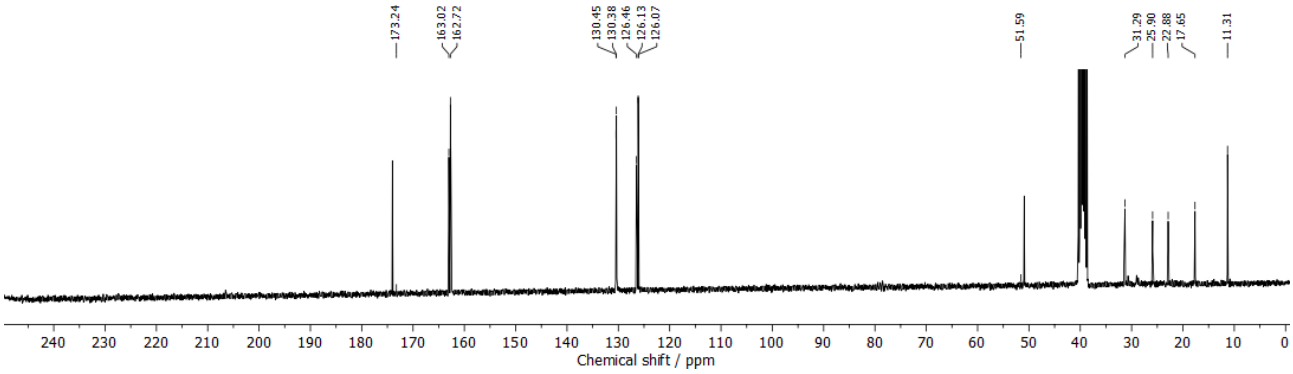
^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 174.0, 162.8 (2C), 130.7, 130.4 (2C), 126.3, 126.3, 126.2, 57.2, 31.3, 24.4, 22.9, 11.2.

HRMS (MALDI) *m/z:* calculated for $C_{23}H_{22}N_2O_6$ $[M]^-$ 422.1483; found 422.1492 (Δ = 2.1 ppm).

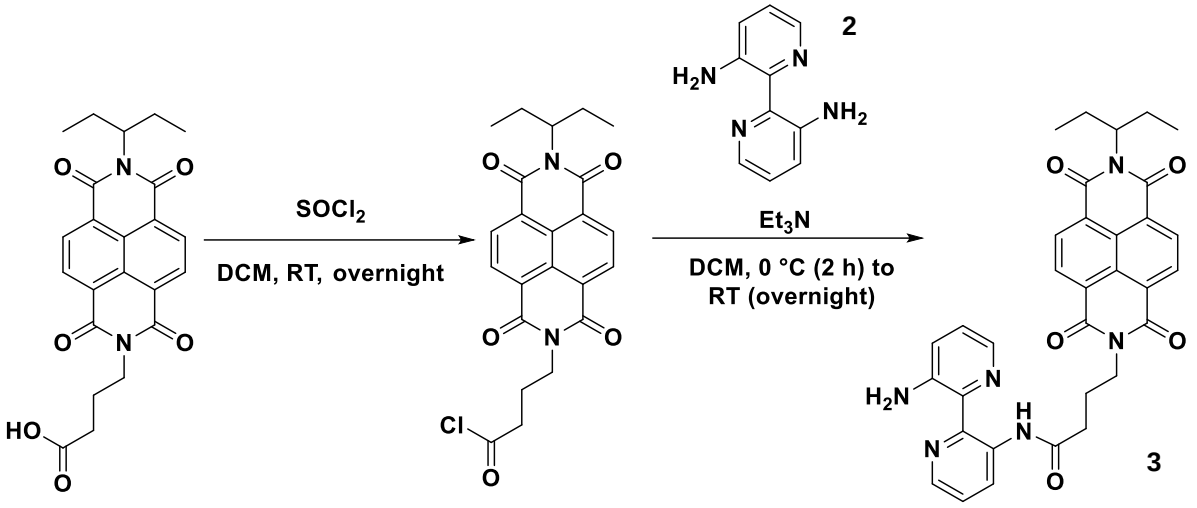
^{1}H NMR (300 MHz, DMSO-D_6)



^{13}C NMR (75 MHz, DMSO-D_6)



Compound **3**.



Dissymmetric NDI **1** (500 mg, 1.18 mmol, 1 eq) was degassed under vacuum/argon atmosphere five times in a Schlenk tube. Then, dry dichloromethane (6 mL) and thionyl chloride (2.57 mL, 35.5 mmol, 30 eq) were added to the powder and the reaction mixture was stirred at room temperature overnight under argon atmosphere. When the reaction was completed, the reagent was completely solubilized. Thionyl chloride was removed by distillation under vacuum. The dissymmetrical chlorinated NDI was dried under vacuum for 4 h before starting the next reaction.

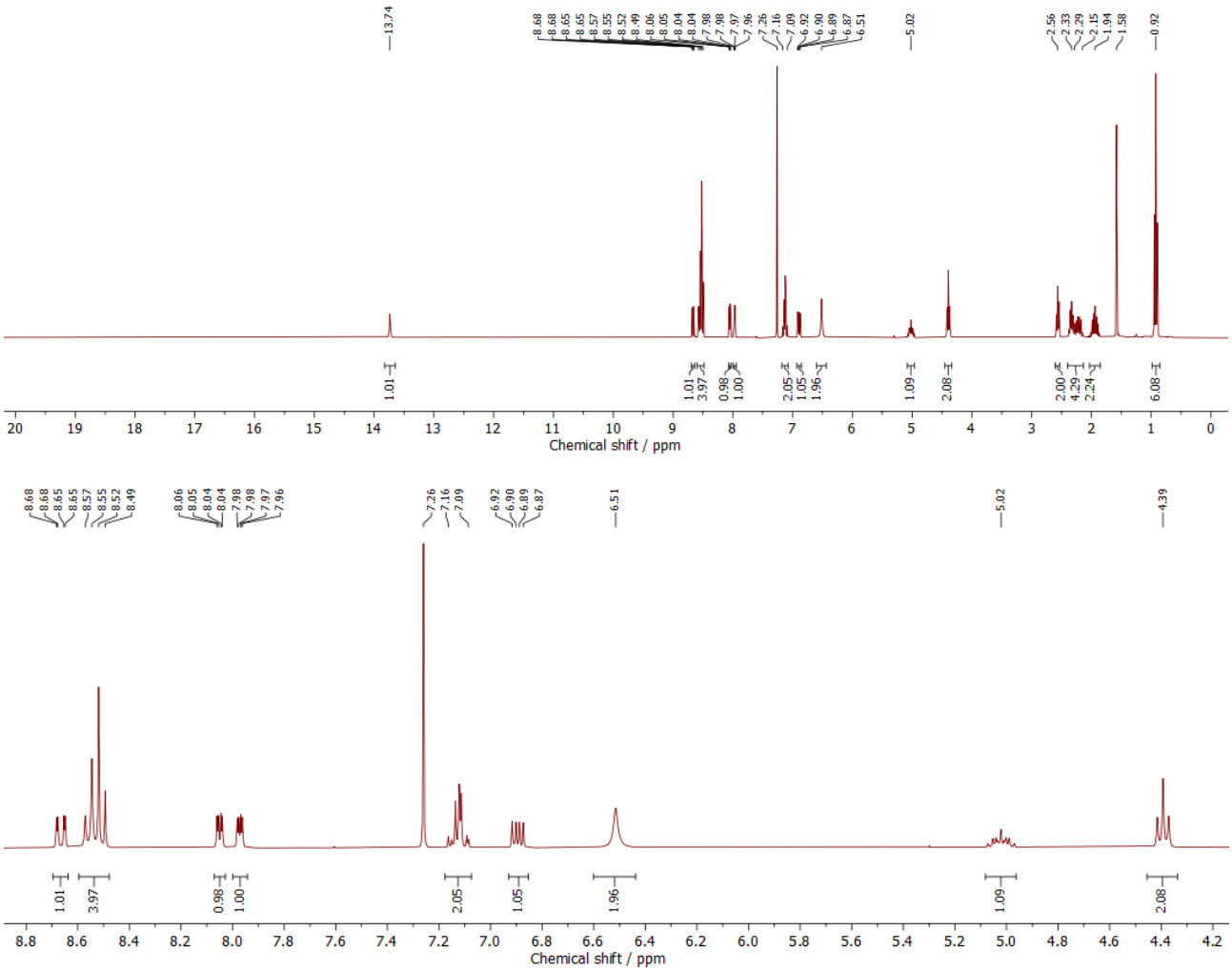
After being degassed under vacuum/argon atmosphere five times, 3,3'-diamino-2,2'-bipyridine (374 mg, 2.01 mmol, 1.7 eq) was solubilized in dry dichloromethane (4.4 mL) and distilled trimethylamine (165 µL, 1.18 mmol, 1 eq). The solution was cooled to 0 °C before adding dropwise the dissymmetrical chlorinated NDI (1.18 mmol, 1 eq) in dry dichloromethane (3.4 mL). The reaction mixture was allowed to stir at 0 °C for 2 h and then at room temperature overnight. A red-brown suspension was formed and the solvent was evaporated *in vacuo*. The crude material was first placed on a short plug of silica (DCM:EtOAc, 85:15) to remove triethylamine before being washed with ethyl acetate several times using the centrifuge (the final compound is not soluble in ethyl acetate contrary to 3,3'diamino-2,2'-bipyridine) to give a red solid (280 mg, 40 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 13.73 (s, 1H, NH), 8.66 (dd, *J* = 8.5, 1.5 Hz, 1H, Py_{ext}), 8.56 (d, *J* = 7.6 Hz, 2H, Ar_{NDI}), 8.50 (d, *J* = 7.6 Hz, 2H, Ar_{NDI}), 8.05 (dd, *J* = 4.6, 1.5 Hz, 1H, Py_{ext}), 7.97 (dd, *J* = 4.0, 1.8 Hz, 1H, Py_{int}), 7.16-7.08 (m, 2H, Py_{int}), 6.89 (dd, *J* = 8.5, 4.6 Hz, 1H, Py_{ext}), 6.51 (s, 2H, NH_2), 5.02 (tt, *J* = 9.5, 5.9 Hz, 1H, $CH_{aminopentane}$), 4.39 (t, *J* = 6.7 Hz, 2H, **CH_2**-N$(CO)_2$), 2.56 (t, *J* = 6.8 Hz, 2H, **CH_2**-CONH), 2.33 (q, *J* = 6.8 Hz, 2H, $CH_{2central}$), 2.28-2.15 (m, 2H, $CH_{2aminopentane}$), 2.01-1.87 (m, 2H, $CH_{2aminopentane}$), 0.92 (t, *J* = 7.5 Hz, 6H, CH_3).

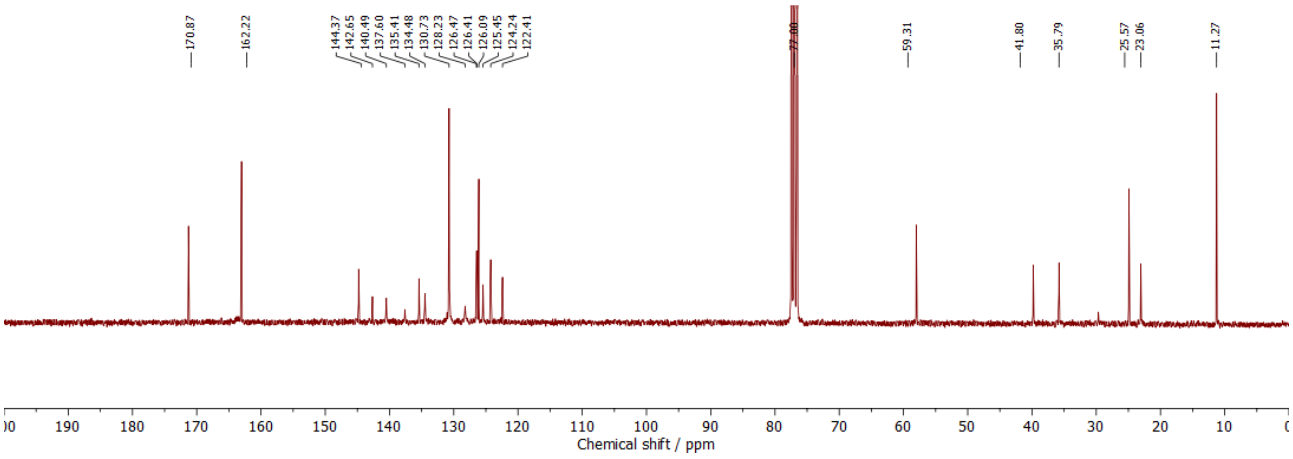
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 163.2 (2C), 145.0, 142.8, 140.7, 137.8, 135.6, 134.6, 130.9 (2C), 128.4, 126.6, 126.6, 126.2 (2C), 125.6, 124.4, 122.6, 58.2, 40.0, 35.9, 25.1, 23.2, 11.4.

HRMS (MALDI) *m/z:* calculated for $C_{33}H_{30}N_6O_5$ $[M]^-$ 590.2283; found 590.2270 (Δ = 2.2 ppm).

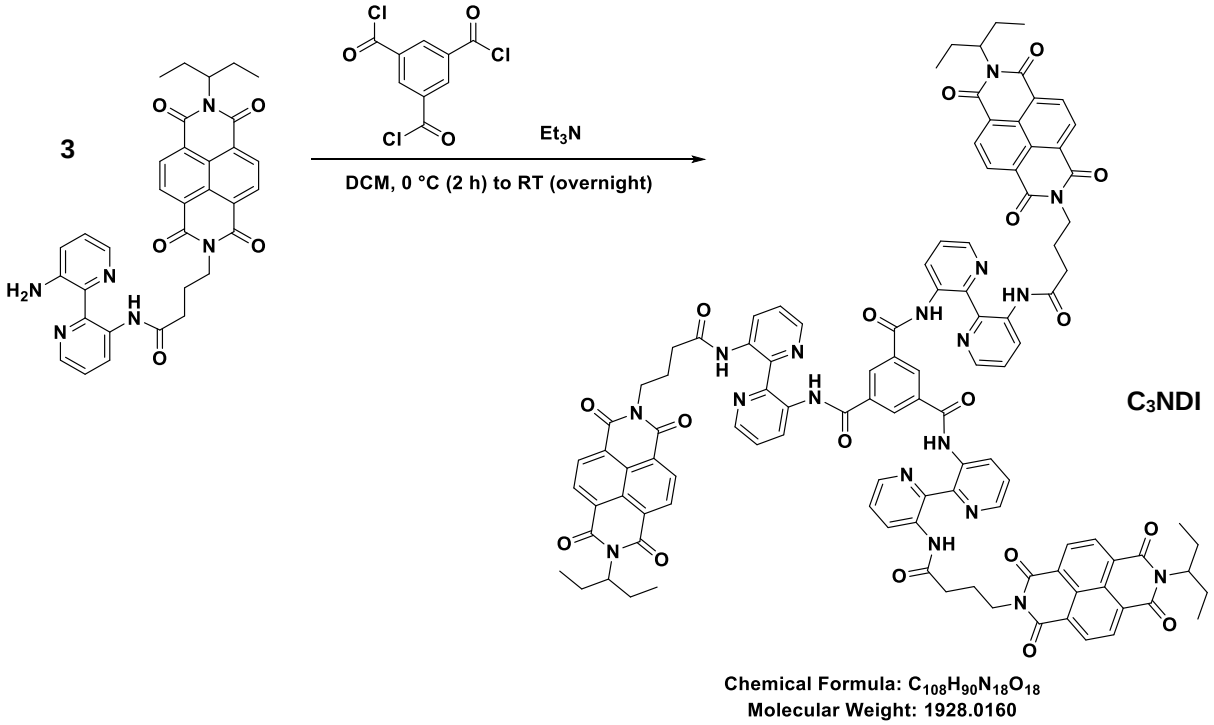
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



C_3NDI



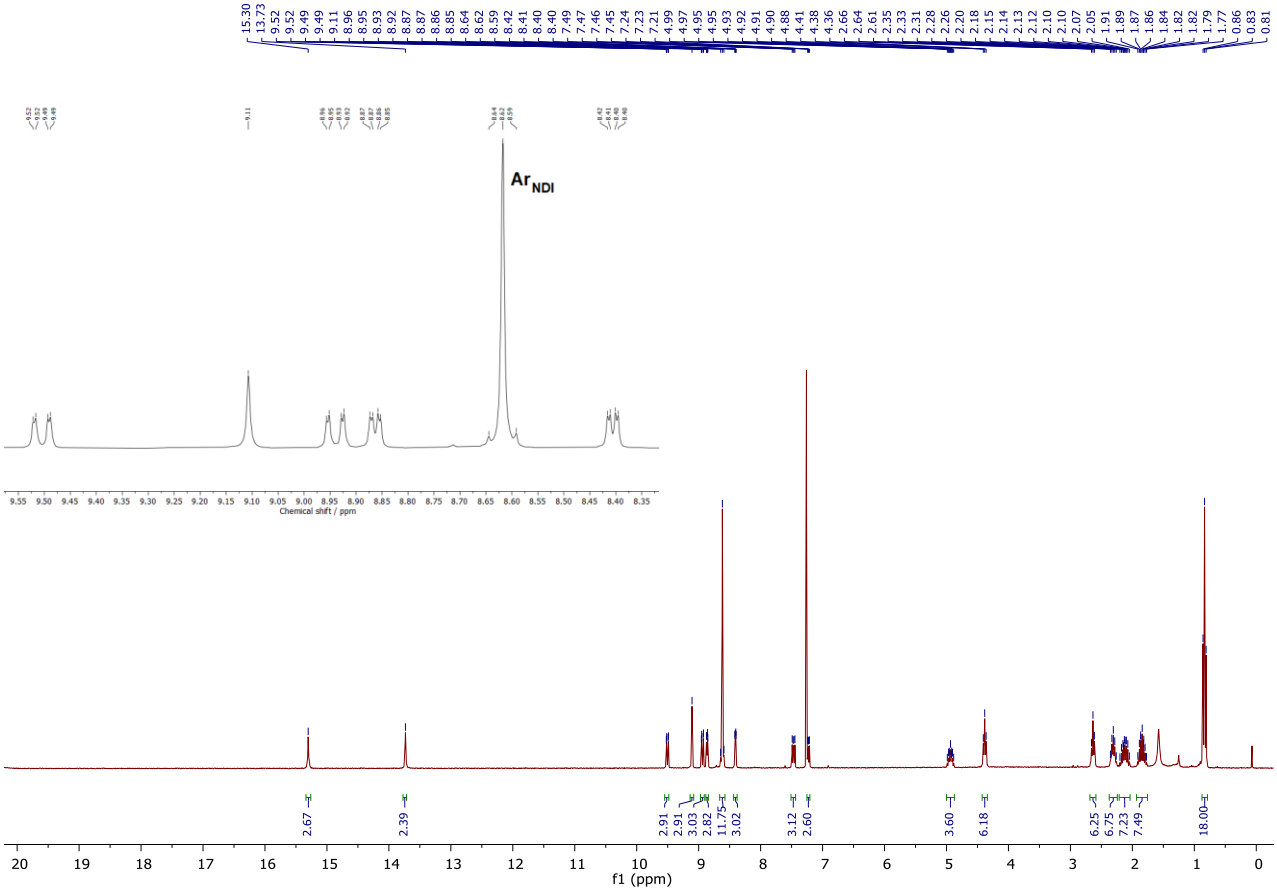
Amine **3** (250 mg, 0.423 mmol, 5 equiv.) was placed into a Schlenk tube and degassed under vacuum/argon atmosphere five times. Dry dichloromethane (5 mL) and distilled triethylamine (59 µL, 0.423 mmol, 5 equiv.) were then added to the powder and the suspension was cooled to 0 °C using an ice bath. In a second Schlenk tube, trimesic acid chloride (22 mg, 84 µmol, 0.2 eq) was dissolved in dry dichloromethane (1 mL) under argon atmosphere and was added dropwise at 0 °C for 20 min in the mixture containing NDI-bipy. When the addition was completed, the reaction mixture was allowed to stir at 0 °C for 2 h and then at room temperature overnight under argon atmosphere. A change of colour from red to orange was observed when the temperature goes from 0 °C to room temperature. The solvent was evaporated *in vacuo* and the crude material was first placed on a short plug of silica gel ($CHCl_3$:EtOH, 96:4) before being injected in chloroform in a recycling preparative HPLC to give an orange-yellow solid (161 mg, 58 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 15.30 (s, 3H, $NH_{interne}$), 13.73 (s, 3H, NH_{ext}), 9.50 (dd, *J* = 8.6, 1.4 Hz, 3H, Py_{ext}), 9.11 (s, 3H, $Ar_{central}$), 8.94 (dd, *J* = 8.5, 1.4 Hz, 3H, Py_{int}), 8.86 (dd, *J* = 4.6, 1.4 Hz, 3H, Py_{int}), 8.63 (d, *J* = 8.1 Hz, 6H, Ar_{NDI}), 8.60 (d, *J* = 7.7 Hz, 6H, Ar_{NDI}), 8.41 (dd, *J* = 4.6, 1.5 Hz, 3H, Py_{ext}), 7.47 (dd, *J* = 8.6, 4.6 Hz, 3H, Py_{ext}), 7.23 (dd, *J* = 8.6, 4.6 Hz, 3H, Py_{int}), 4.93 (tt, *J* = 9.6, 6.0 Hz, 3H, $CH_{aminopentane}$), 4.38 (t, *J* = 6.9 Hz, 6H, **CH_2**-$N(CO)_2$), 2.64 (t, J = 7.1 Hz, 6H, **CH_2**-CONH), 2.31 (q, *J* = 7.0 Hz, 6H, $CH_{2central}$), 2.20-2.05 (m, 6H, $CH_{2aminopentane}$), 1.91-1.77 (m, 6H, $CH_{2aminopentane}$), 0.83 (t, *J* = 7.4 Hz, 18H, CH_3).

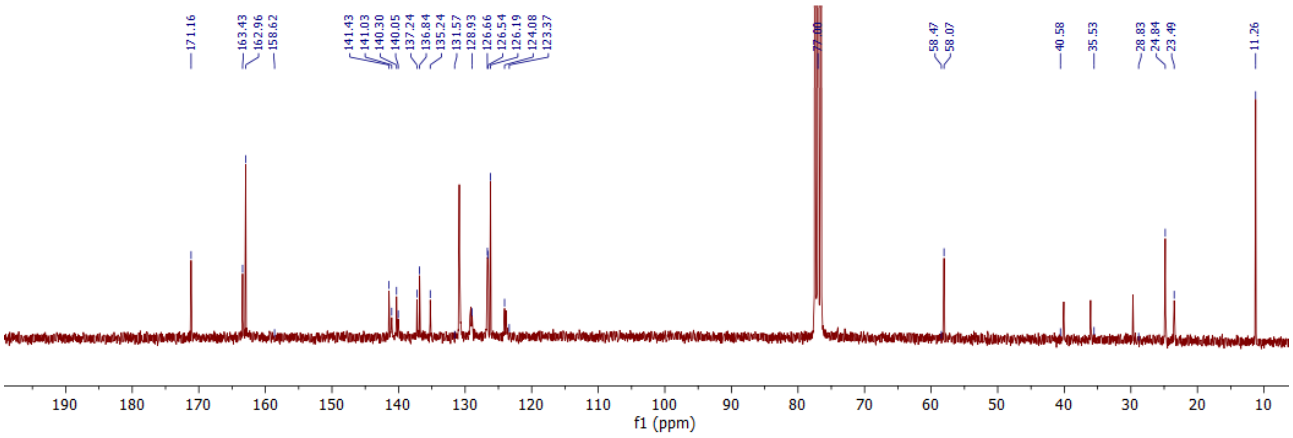
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 163.7, 163.1 (2C), 141.7, 141.2, 140.5, 140.3, 137.4, 137.0, 135.5, 131.0 (2C), 129.5, 129.4, 129.2, 126.8, 126.7, 126.4 (2C), 124.3, 124.0, 58.2, 40.2, 36.2, 25.0, 23.7, 11.4.

HRMS (MALDI) *m/z:* calculated for $C_{108}H_{91}N_{18}O_{18}$ $[M+H]^+$ 1927.6753; found 1927.6788 (Δ = 1.82 ppm).

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



Reference

S1) C. R. Rice, S. Onions, N. Vidal, J. D. Wallis, M.-C. Senna, M. Pilkington and H. Stoeckli-Evans, *Eur. J. Inorg. Chem.*, **2002**, 1985.