Supporting Information

Retention of Perylene Diimide Optical Properties in Solid-State Materials Through Tethering to Nanodiamonds

Asia R. Y. Almuhana, Philipp Langer, Sarah, L. Griffin, Rhys W. Lodge, Graham A. Rance and Neil R. Champness

Experimental

Materials and characterisation

All chemicals were obtained from commercial suppliers (Alfa Aesar, Fisher Scientific, Sigma-Aldrich) and used without further purification. Nanodiamonds (produced by laser ablation) were provided by Ray Technologies Ltd. (Israel).[S1,S2] Column chromatography was performed on silica gel (Merck silica gel 60, 0.2 - 0.5 mm, 50 - 130 mesh). Preparative thin layer chromatography (TLC) was also employed, using silica gel as the stationary phase on plates purchased from AnalTech. Thin layer chromatography were used to monitor the progress of the reactions, using silica gel as the stationary phase on an aluminium substrate. Reactions sensitive to air and moisture were carried out using a standard Schlenk line, with dinitrogen as the inert gas. Glassware was flame-dried under vacuum and backfilled with dinitrogen.

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained at room temperature with either a Bruker DPX (400 MHz) a Bruker AV(III) (400 MHz) or a Bruker 500 MHz spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane (TMS) using the $CDCl_3$ residual peak at 7.26 ppm (^{1}H), 77.00 ppm (^{13}C) as reference. Matrix-assisted laser desorption ionisation – time-of-flight (MALDI-TOF) mass spectrometry was performed using a Bruker Ultraflex III mass spectrometer, with a matrix solution of trans-2-[3-(4-tert, butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) ($m/z = 250.3$). Infrared spectra were recorded using a Brucker Tensor 27 FTIR spectrometer in the solid state between two KBr discs and recorded in the 400-4000 cm^{-1} range at room temperature (with an ATR attachment as appropriate). Ultraviolet-visible spectroscopy (UV/Vis) was carried out using a PerkinElmer Lambda 25 UV/Vis spectrometer in 1 cm length quartz cuvettes with a wavelength range from 190 to 1100 nm. DLS measurements were performed using a Malvern Zetasizer Nano-ZS. ND samples were dispersed in chloroform with ultrasonication for 10 min prior to analysis. Raman and fluorescence spectra were obtained using a HORIBA LabRAM HR Raman microscope (325 or 532 nm laser excitation). Transmission electron microscopy was carried out using JEOL 2100F FEG-TEM with an accelerating voltage of 200 kV (information limit of 0.19 nm). EDX spectroscopy was carried out using an Oxford Instruments 80 mm X-Max system. Samples were prepared for TEM and EDX by casting several drops of methanolic suspension onto copper-grid mounted “holey” carbon films.

The following compounds were prepared according to literature procedures, or small adaptations thereof: dibromo-3,4,9,10-perylenetetracarboxylic dianhydride,[S3] *N,N'*-di(5-hydroxypentyl)-1,7-dibromoperylene-3,4:9,10-perylenetetracarboxylic diimide,[S4] *N,N'*-di(5-hydroxypentyl)-1,6- dibromoperylene-3,4:9,10- perylenetetracarboxylic diimide,[S4] *N*-(2,6-bis(diphenylmethyl)-4-methylphenyl)-perylene-3,4 dicarboximide-9,10-anhydride (**2a**),[S5] **ND-COOH**,[S6] *N,N'*-di(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide.[S7]

*Synthesis of N,N'-di(5-hydroxypentyl)-1,7-dimorphlinoperylene-3,4:9,10-perylenetetracarboxylic diimide (**1a**) and N,N'-di(5-hydroxypentyl)-1,6- dimorpholinoperylene-3,4:9,10-perylenetetracarboxylic (**1b**):* The synthesis of **1a** and **1b** was carried out according to an adaptation of a literature procedure.[S8] A mixture of *N,N'*-di(5-hydroxypentyl)-1,7-dibromoperylene-3,4:9,10-perylenetetracarboxylic diimide and *N,N'*-di(5-hydroxypentyl)-1,6- dibromoperylene-3,4:9,10- perylenetetracarboxylic diimide (0.500 g, 0.684 mmol) was dissolved in excess morpholine (20 mL) and heated to 65 °C for three days. The mixture was cooled to room temperature, slowly poured into HCl (2 M) and extracted with chloroform. The organic phase was washed twice with HCl (2 M) and once with water before being dried over $MgSO_4$, and then filtered. The solvent was removed on a rotary evaporator and the crude product purified by column chromatography (silica, DCM: Methanol 97:3) to afford the 1,7-isomer, **1a**, as a green microcrystalline powder (0.300 g, 1.74 mmol, 62 %) and the 1,6-isomer, **1b**, as a blue powder (60 mg, 12 %).

(**1a**): MS (MALDI-TOF): m/z^- = 732.3 ($C_{42}H_{44}N_4O_8$ $[M]^-$ requires 732.3). ^1H NMR (400 MHz, $CDCl_3$): δ/ppm 9.59 (d, *J*=8.28 Hz, 2 H), 8.38 (d, *J*=8.28 Hz, 2 H), 8.24 (s, 2 H), 4.25 (t, *J*=7.40 Hz, 4 H), 3.85 - 3.98 (m, 8 H), 3.71 (t, *J*=6.40 Hz, 4 H), 3.33 (d, *J*=11.92 Hz, 4 H), 3.02 (t, *J*=9.79 Hz, 4 H), 1.83 (quin, *J*=7.47 Hz, 4 H), 1.67 - 1.75 (m, 4 H), 1.51 - 1.59 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm 163.6, 150.1, 135.0, 130.0, 128.4, 124.6, 123.9, 123.1, 123.0, 122.9, 121.5, 66.7, 63.0, 51.7, 40.8, 32.7, 28.1, 23.6. IR (ATR): ν/cm^{-1} 3441, 2938, 2859, 1689, 1648, 1593, 1297, 1116, 809, 720.

(**1b**): MS (MALDI-TOF): m/z^- = 732.3 ($C_{42}H_{44}N_4O_8$ $[M]^-$ requires 732.3). ^1H NMR (400 MHz, $CDCl_3$): δ/ppm 9.90 (d, *J*=8.3 Hz, 2 H), 8.65 (d, *J*=8.3 Hz, 2 H), 8.41 (s, 2 H), 4.21 - 4.30 (m, 4 H), 3.89 - 4.02 (m, 8 H), 3.71 (t, *J*=5.55 Hz, 4 H), 3.31 (d, *J*=11.84 Hz, 4 H), 3.04 - 3.18 (m, 4 H), 1.78 - 1.88 (m, 4 H), 1.67 - 1.73 (m, 4 H), 1.50 - 1.58 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ/ppm 163.5, 152.1, 135.4, 130.7, 128.8, 124.3, 123.5, 122.0, 120.8, 66.5, 62.7, 51.7, 40.9, 31.9, 29.7, 22.7, 14.1. IR (FTR): ν/cm^{-1} 3441, 2936, 2857, 1698, 1659, 1591, 1297, 1125, 809, 747.

*Synthesis of 2-(2,6-dibenzhydryl-4-methylphenyl)-9-(5-hydroxypentyl)-3,4:9,10-perylenetetracarboxylic diimide (**2**):* A flame-dried 2-neck flask was purged 3 times with N_2 and charged with **2a** (0.08 g, 0.0984 mmol), imidazole (4.5 g) and 5-amino-1-propanol (0.0112 g, 0.108 mmol). The mixture was heated to 130 °C for 2 h. The dark red reaction mixture was dissolved in chloroform (100 mL) and washed with water (3 x 50 mL) and brine (2 x 50 mL) before being dried over anhydrous $MgSO_4$, the solvent was then reduced under pressure. The mixture was separated by column chromatography first column: (silica, methanol: chloroform

[1:100]), however the first fraction was a mixture of product and starting material only. This mixture was separated successfully by further column chromatography, second column: (silica, acetone: chloroform 0.1:100). To give the pure product as a fluorescent red solid (0.051 g, 0.063 mmol, 57 %).

MS (MALDI-TOF): m/z^- 898 ($C_{62}H_{46}N_2O_5$ [M^-] requires 898.3). ^1H NMR (400 MHz, $CDCl_3$): δ/ppm 8.68 (dd, *J* = 24 Hz *J* = 8 Hz, 4 H), 8.47 (dd, *J* = 92 Hz, *J* = 8 Hz, 4 H), 7.12-7.14 (m, 12 H), 6.99-7.01 (m, 8 H), 6.78 (s, 2 H), 5.35 (s, 2 H), 4.25 (t, *J* = 8 Hz, 2 H), 3.70 (t, *J* = 6 Hz, 2 H), 2.25 (s, 3 H), 1.84 (quin, *J* = 8 Hz, 2 H), 1.70 (quin, *J* = 7 Hz, 2 H), 1.55 (quin, *J* = 6 Hz, 2 H). ^{13}C NMR (75 MHz; $CDCl_3$): δ/ppm 163.54, 162.31, 142.23, 142.17, 138.07, 134.96, 134.57, 131.54, 131.36, 131.32, 129.66, 129.29, 129.51, 129.46, 128.62, 128.15, 126.62, 126.28, 123.38, 123.19, 123.09, 123.03, 62.81, 52.60, 40.49, 32.41, 27.89, 23.33, 21.81 ppm. IR (ATR): ν/cm^{-1} 3535, 2926, 2926, 1709, 1656, 1592, 1357, 1337.

Synthesis of ND-PDI Composites, ***ND-1a, ND-1b*** *and* ***ND-2****:* A flame-dried 2-neck flask was purged 3 times with N_2 and charged with **ND-COOH** (30 mg), 0.02 mmol of perylene (**1a**, **1b** 14 mg or **2** 18 mg), N, N′-dicyclohexylcarbodiimide, DCC, (5 mg, 0.02 mmol) and 4-dimethylaminopyridine (1 mg, 0.01 mmol). Anhydrous acetonitrile (10 mL) was added and the mixture was sonicated for 45 min. The well dispersed, dark red mixture was stirred at RT under nitrogen for 48 h. The mixture was separated by centrifugation at 10,000 rpm, purified through consecutive wash/sonication/centrifugation cycles with acetonitrile (x3), ethanol (x1) and chloroform (x6). The PDI-terminated nanodiamonds were filtered under reduced pressure through a polycarbonate membrane (pore size: 0.2 µm) and washed with chloroform (20 mL) before being oven dried at 50 °C for 24 h.

ND-1a: green powder. IR (FTR) : ν/cm^{-1} 3415, 2950, 2919, 1732, 1635, 1579, 1542, 1466, 1383, 1140, 1118. Fluorescence (solid): λ/nm 763.

ND-1b: blue powder. IR (FTR): ν/cm^{-1} 3440, 2922, 2851, 1700, 1630, 1541, 1441, 1384, 1116. Fluorescence (solid): λ/nm 775.

ND-2: red powder. IR (FTR): ν/cm^{-1} 3432, 2900, 1733, 1638, 1541, 1441, 1391, 1113. Fluorescence (solid): λ/nm 585, 545.

Additional characterisation of PDIs

*Single crystal structure of **1a**.*

Single crystal X-ray diffraction experiments were performed on a XtalLAB PRO MM007, PILATUS3 R 200K diffractometer at 120 K using monochromated Cu Kα radiation (λ = 1.5418 Å). The structures were solved by direct methods using SHELXS or SHELXT[S9] and refined with SHELXL[S10] using a least squares method. OLEX2 software was used as the solution, refinement and analysis program.[S11] All hydrogen atoms were placed in geometrically calculated positions; non-hydrogen atoms were refined with anisotropic displacement parameters. In specific cases geometric restraints were applied. Details of dealing with disorder and other refinement are described in the corresponding, deposited cif, CCDC 2085715 (**1a**). Disordered solvent molecules could not be sensibly modelled to give convergence and the data was treated with PLATON SQUEEZE,[S12] which gave an estimate of 182 electrons per cell, corresponding to approximately 3 molecules of chloroform per unit.

Crystal Data for **1a**: $C_{21}H_{22}N_2O_4$ (M = 366.40 g/mol): tetragonal, space group P-42c (no. 112), $a = b$ = 15.7322(5), c = 15.2594(7) Å, V = 3776.7(3) Å^3, Z = 8, T = 120(2) K, μ(CuKα) = 0.734 mm-1, D_{calc} = 1.289 g/cm^3, 11149 reflections measured, 3570 unique (Rint = 0.0493) which were used in all calculations. The final R1 was 0.0727 (I > 2σ(I)) and wR2 was 0.2141 with GOF = 1.136.

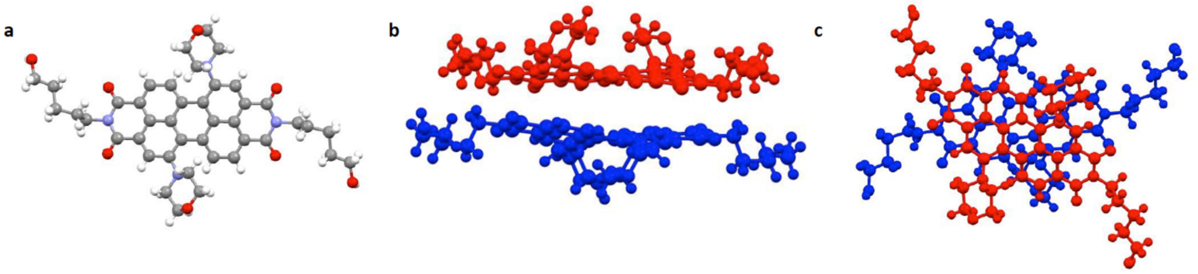

***Figure S1**. Views of the single crystal X-ray structure of **1a**. (a) The structure of **1a** confirming the 1,7-subsitution pattern (carbon – grey; oxygen – red; nitrogen – blue; hydrogen – white); (b and c) stacking of two adjacent molecules of **1a** in the solid-state structure, (b) view parallel to stacking and (c) view perpendicular to stacking. Adjacent molecules are shown in red and blue to aid the reader.*

Additional characterisation of NDs

Raman spectra of ND and ND-COOH

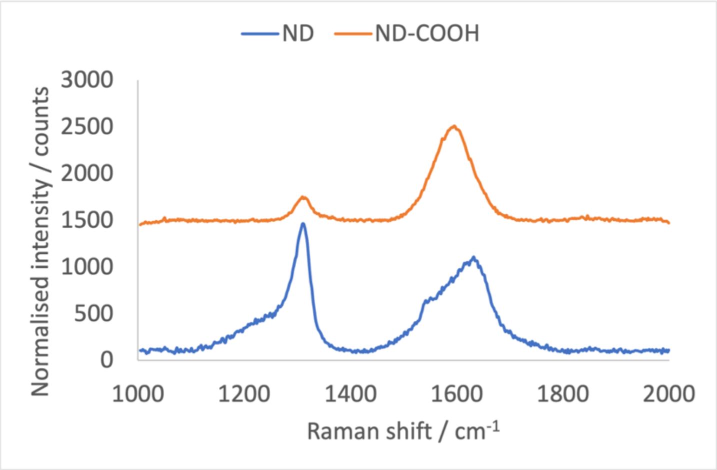

Figure S2**. The 325 nm Raman spectra of pristine* **ND** *(blue) and oxidised nanodiamonds* ***ND-COOH *(orange). The peak at ~1315 cm^{-1} in both spectra is consistent with the triply degenerate zone-centre optical phonon with F_{2g} symmetry found in diamond. The peak at ~1597 cm^{-1} is the characteristic G-band associated with sp^2-hybridised carbon nanostructures. The peak at ~1630 cm^{-1} is a combination of an O-H bend and C=C stretching vibration; it reduces in intensity (relative to the G-band) after oxidation and suggests that (i) non-carboxylic acid functional groups were removed or converted to acid groups during acid treatment, and (ii) that sp^2-hybridised carbon has not been lost during this treatment.*

IR spectra of ND and ND-COOH

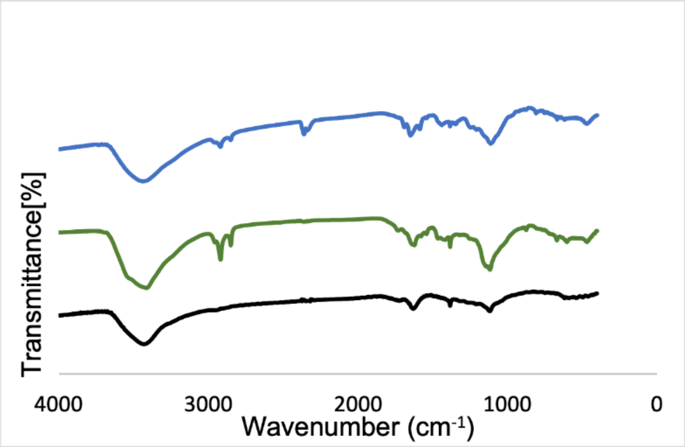

Figure S3. *IR spectra of* ***ND-COOH*** *(black),* ***ND-1a*** *(green) and* ***ND-1b*** *(blue). The observation of a broad peak at 3415 cm^{-1} is consistent with an OH stretching mode of the carboxylic acid groups in* ***ND-COOH****. Its presence subsequent to reaction with PDI can be rationalised by residual carboxylic acids in the ND-PDI species, or potentially unreacted pendent alcohols in* ***ND-1a*** *or* ***ND-1b****.*

Thermogravimetric analysis of ND-COOH and ND-PDIs

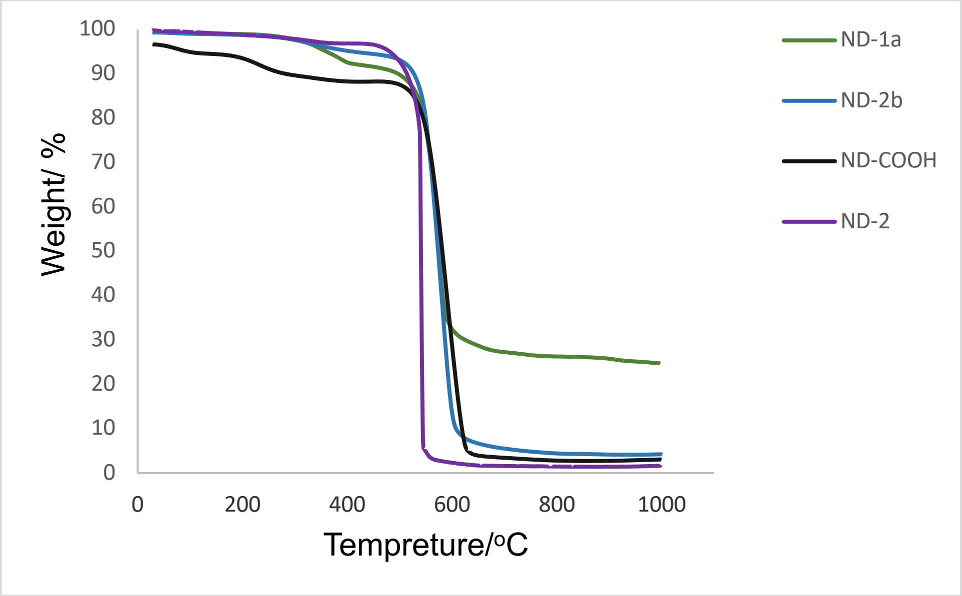

Figure S4. *Thermogravimetric analysis of **ND-1a** (green), **ND-1b** (blue), **ND-2** (purple) and **ND-COOH** (black) as a comparison. Any loss in weight that occurred below 115 °C was attributed to adsorbed water.*

EDX spectra of ND-COOH

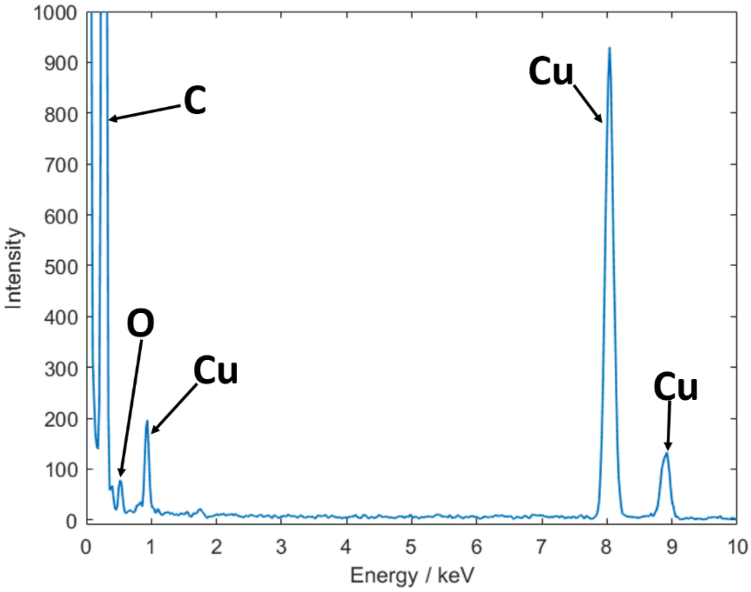

Figure S5. *EDX spectrum of **ND-COOH**. Note: Cu peaks are due to the copper mesh of the TEM grid.*

DLS analysis of ND, ND-COOH and ND-PDIs

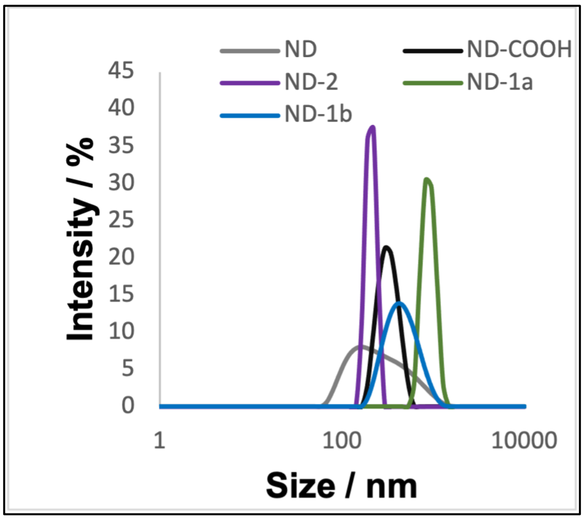

Figure S6. *DLS analysis of:* ***ND*** *(grey)* d_H *= 98±22, 274 ±125 and 790 ± 272 nm (multimodal):* ***ND-COOH*** *(black)* d_H *= 301±80 nm;* ***ND-1a*** *(green)* d_H *= 873±142;* ***ND-1b*** *(blue)* d_H*= 479±188 nm; and* ***ND-2*** *(purple)* d_H *= 219±77 nm.*

Fluorescence spectroscopy analysis of PDIs and ND-PDIs

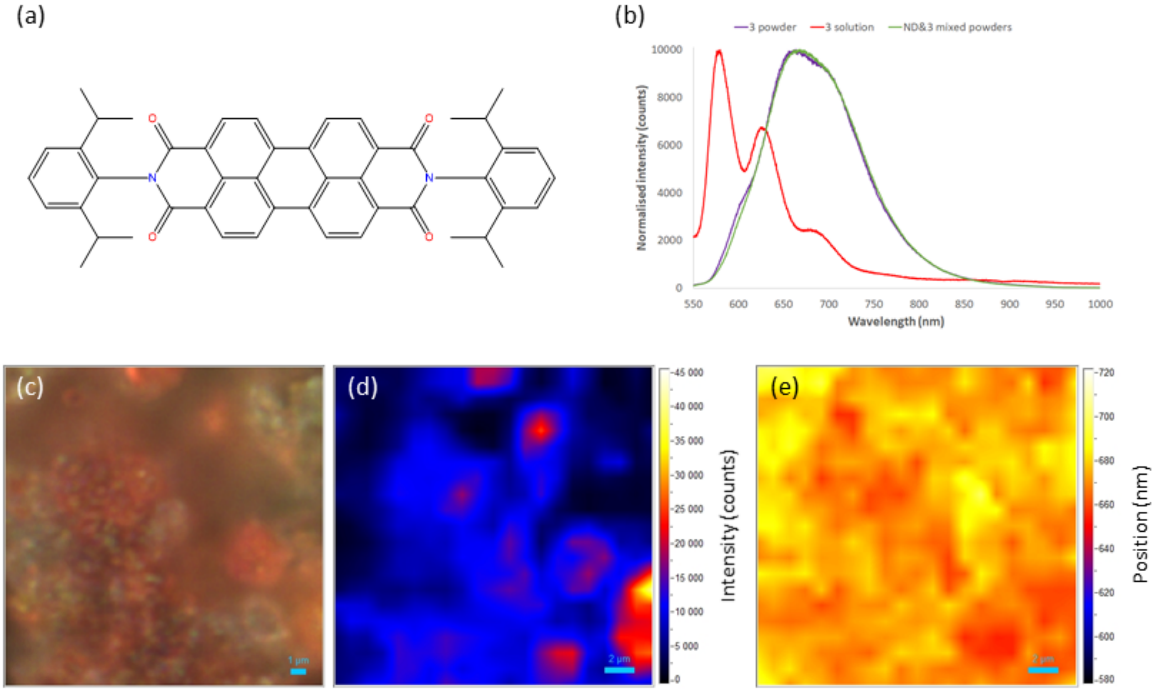

Figure S7. *(a) The structure of the 2,6-diisopropylphenyl-substituted PDI (**3**), chosen for control measurements owing to its inability to form ester linkages with surface functional groups of **ND-COOH**. (b) Normalised fluorescence spectra of **3** as solid powder, in acetonitrile solution and as mechanical mixture with **ND-COOH** (powders ground in a 1:1 mass ratio for 5 minutes in a pestle and mortar), indicating that the mechanical mixture more closely resembles the parent PDI powder than the solution. (c) An optical image of the mechanical mixture of **ND-COOH** and **3** and corresponding fluorescence maps (20x20 µm in 1 µm steps) displaying (d) the intensity (as peak height) and (e) the position of the emission maximum. The optical micrograph indicates that the mixed powder contains micron-sized crystalline domains of the two components, which can be readily discriminated by their peak intensity in (d). However, the relative position of the emission maximum (e)* *within the spectral range 565-785 nm, and the shape of the spectral profile, is highly consistent with that seen in the parent PDI powder spectrum, throughout the entirety of the mapped area. This provides further evidence that simple mechanical mixing of NDs and PDIs does not create the required physical separation of PDIs observed when chemically grafting PDIs to NDs to induce solution-phase optical behaviour in solid-state materials.*

References

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