SUPPLEMENTARY INFORMATION

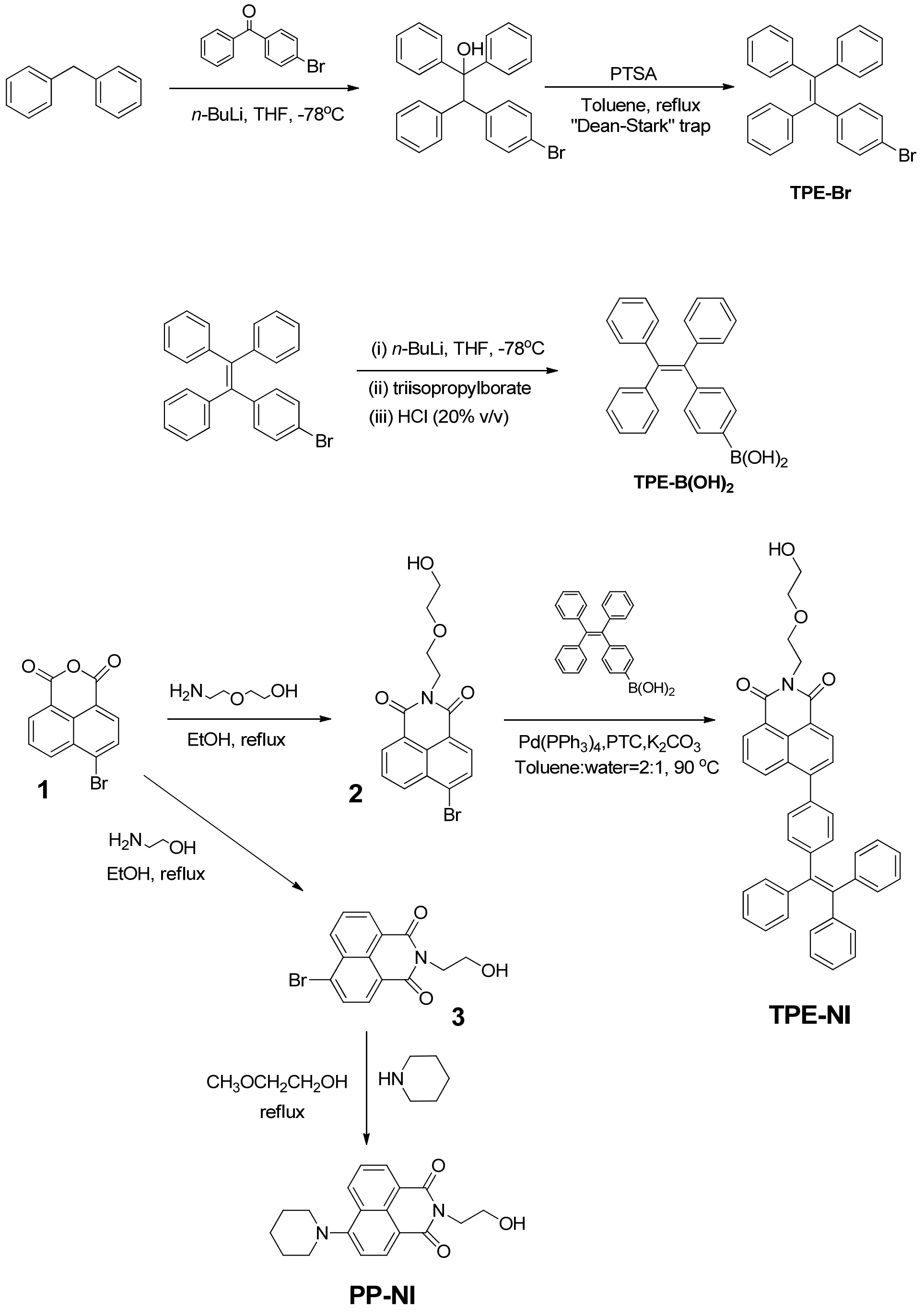
Utilising tetraphenylethene as a dual activator for intramolecular charge transfer and aggregation induced emission

Guo-Feng Zhang, Matthew P. Aldred,* Wen-Liang Gong, Chong Li and Ming-Qiang Zhu*

CONTENTS

1. EXPERIMENTAL.

SYNTHESIS SCHEME:



Scheme 1. Synthesis route to TPE-NI and PP-NI.

1(a) INSTRUMENTATION.

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Aladdin, Acros Organics and Puyang Huicheng Chemical Co. Ltd. All reactions were carried out under a dry nitrogen atmosphere and the temperatures were measured externally. THF was dried using sodium wire and benzophenone indicator. Reported yields are isolated yields. Purification of all final products was accomplished by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot (visualised using UV-light at 254 nm and 365 nm) was obtained. The purity of all final materials was further confirmed quantitatively by HPLC. ^{1}H NMR spectra are reported in parts per million (PPM) relative to tetramethylsilane as an internal standard. Fluorescence microscope images of TPE-NI; samples prepared from a 90% water-THF solvent mixture dropped casted onto glass slides and the solvent evaporated. Performed with a home-built TIRF microscope setup consisting of an Olympus IX 71 inverted microscope, a 100x/NA1.49 oil immersion TIRF objective (UAPON 100XOTIRF, Olympus), a 405 nm laser diode and a 561 nm diode-pumped solid-state laser (both from CNILaser, China), and an Andor iXon 897 EMCCD camera. The relative fluorescence quantum yields in all 13 solvents were estimated using 2 standard materials, namely; (1) quinine sulphate (in 0.1M H_2SO_4) and (2) 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) (in ethanol). For this calculation a good overlap in absorption and emission between the standard and the “unknown” fluorphore (i.e., TPE-NI) is crucial. It can be seen from the absorption and emission spectra that although the absortion maxima changes only slightly there is a large change in emission maxima. Therefore, one universal standard that overlaps both the absorption and emission for TPE-NI in all 13 solvents was not possible, therefore two standards were needed. After careful experimentation, we found that quinine sulphate and DCM were ideal standards for the lower polarity and higher polarity solvents, respectively, in which its absorption and emission spectra overlapped nicely with TPE-NI. UV-VIS: Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600), PL: Edinburgh instruments (FLSP920 spectrometers), ^{1}HNMR: (Bruker AV400), Mass Spectrometry: Agilent (1100 LC/MSD Trap), Fluorescence Microscopy: Olympus BX61, Dynamic Light Scattering: Malvern Instruments ZS90.

1(b) SYNTHESIS PROCEDURES.

The compounds 6-bromo-2-(2-(2-hydroxyethoxy)ethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**2**)[1] , 4-(1,2,2-triphenylvinyl)phenylboronic acid (**3**)[2] were prepared according to the previous literature with slight modifications.

6-Bromo-2-(2-(2-hydroxyethoxy)ethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (2)

A mixture of 6-bromobenzo[de]isochromene-1,3-dione (**1**, 10 g, 36 mmol), 2-(2-aminoethoxy)ethanol (3.8 g, 36 mmol) in 200 ml ethanol was heated to reflux for 2h, and cooled down to room temperature. The precipitation was collected by filtration and dried in the oven over night to get the final product(11.25 g, 85.8 %).
^{1}HNMR (400 MHz, $CDCl_3$): δ 3.66 (m, 8H), 3.84 (t, 3H), 4.42 (t, 3H), 7.83 (t, 1H), 8.03 (d, 1H, J= 7.6 Hz), 8.41 (d, 1H, J= 7.6 Hz), 8.56 (d, 1H, J = 8.8 Hz), 8.67 (d, 1H, J = 8.8 Hz).
MS m/z (APCI): $[M+1]^+$: 365.8.

2-(2-(2-Hydroxyethoxy)ethyl)-6-(4-(1,2,2-triphenylvinyl)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (TPE-NI)

A mixture of 6-bromo-2-(2-(2-hydroxyethoxy)ethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**2**, 0.52 g, 1.42 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**TPE-B(OH)$_2$**, 0.61 g, 1.62 mmol), K_2CO_3 (19 mg, 0.14 mmol), toluene (20 ml), water (10 ml) and tetrabutylammonium hydrogen sulfate (0.05 g, 0.14 mmol) was added and the system was flushed with nitrogen. $Pd(PPh_3)_4$ (75 mg, 0.07 mmol) was added and the reaction mixture was stirred under nitrogen for 12 hours at 90 ^{o}C. After cooling down, the reaction mixture was extracted with DCM, washed with water three times, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was chromatographed on silica gel eluting with DCM/MeOH (20:1) to yield a yellow solid (0.76 g, 88.3 %).
^{1}HNMR (400 MHz, d_6-DMSO): δ3.46 (m, 4H), 3.64 (t, 2H), 4.21 (t, 2H), 7.0-7.20 (m, 17 H), 7.26 (d, 2H , J = 8.0 Hz), 7.67 (d, 1H, J = 8.4 Hz), 7.77 (t, 1H), 8.04 (d, 1H, J = 8.4 Hz), 8.45 (m, 2H).
MS m/z (APCI): $[M+1]^+$ 616.3.
Elemental analysis, expected (%): C 81.93, H 5.40, N 2.27, O 10.39, obtained (%): C 81.56, H 5.34, N 2.42, O 10.38.

6-Bromo-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (3)

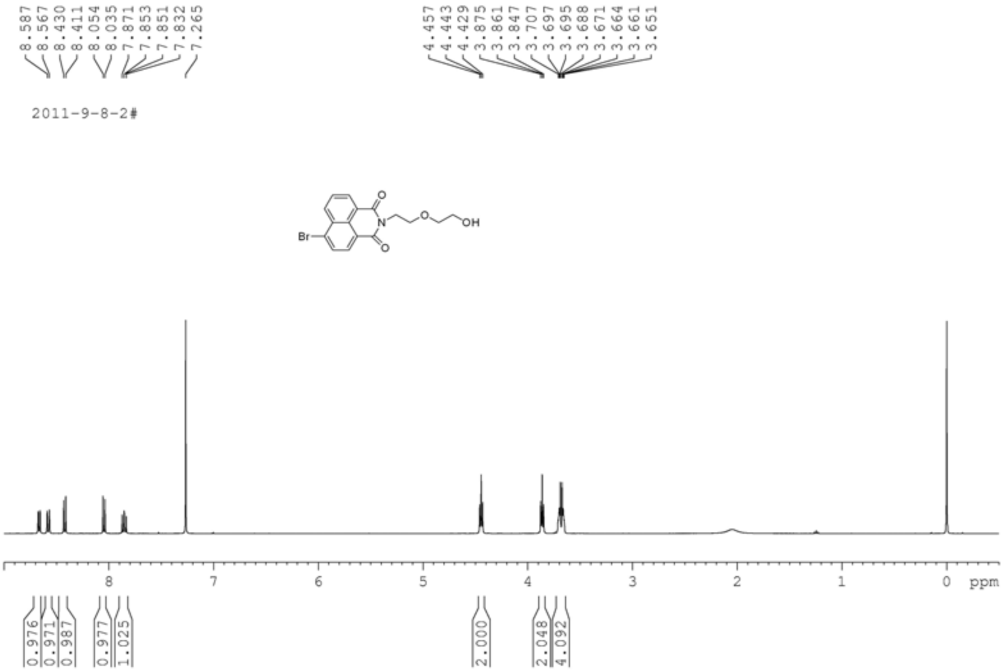
A mixture of 6-bromobenzo[de]isochromene-1,3-dione (**1**, 10 g, 36 mmol), 2-aminoethanol (2.2 g, 36 mmol) in 200 ml ethanol was heated to reflux for 2h, and cooled down to room temperature. The resulting precipitate was collected by filtration and dried in the oven over night to yield the final product (8.76 g, 76 %).
^{1}HNMR (400 MHz, $CDCl_3$): δ 2.19 (b, 1H), 3.99 (t, 2H), 4.45 (t, 2H), 7.84 (t, 1H), 8.05 (d, 1H, J = 8.0 Hz), 8.42 (d, 1H, J = 8.0 Hz), 8.58 (d, 1H, J = 7.6 Hz), 8.66 (d, 1H, J = 7.2 Hz).

2-(2-Hydroxyethyl)-6-(piperidin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (PP-NI)

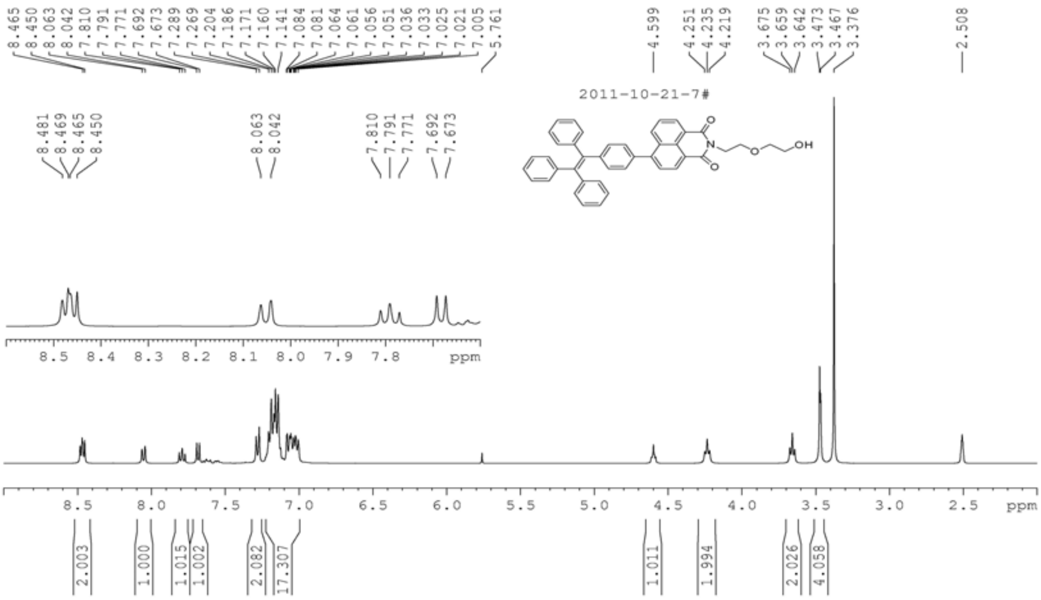
A mixture of 6-bromo-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**3**, 6.4 g, 20 mmol), piperidine (3.4 g, 40 mmol) in 2-methoxyethanol (25 ml) was heated to reflux overnight, and cooled down to room temperature and concentrated under reduced pressure. The crude product was precipitated and recrystallised in ethanol to yield a yellow solid (4.86 g, 75 %).
^{1}HNMR (400 MHz, $CDCl_3$): δ 1.74 (m, 2H), 1.89 (m, 4H), 2.65 (b, 1H), 3.25 (t, 4H), 3.98 (s, 2H), 4.46 (t, 2H), 7.18 (d, 1H, J = 8.0 Hz), 6.68 (t, 1H), 8.41 (d, 1H, J = 8.4 Hz), 8.51 (d, 1H, J = 8.0 Hz), 8.59 (d, 1H, J = 8.4 Hz).
MS m/z (APCI): $[M+1]^+$: 324.9

2. ^{1}H-NMR SPECTRA.

COMPOUND **2**



COMPOUND **TPE-NI**



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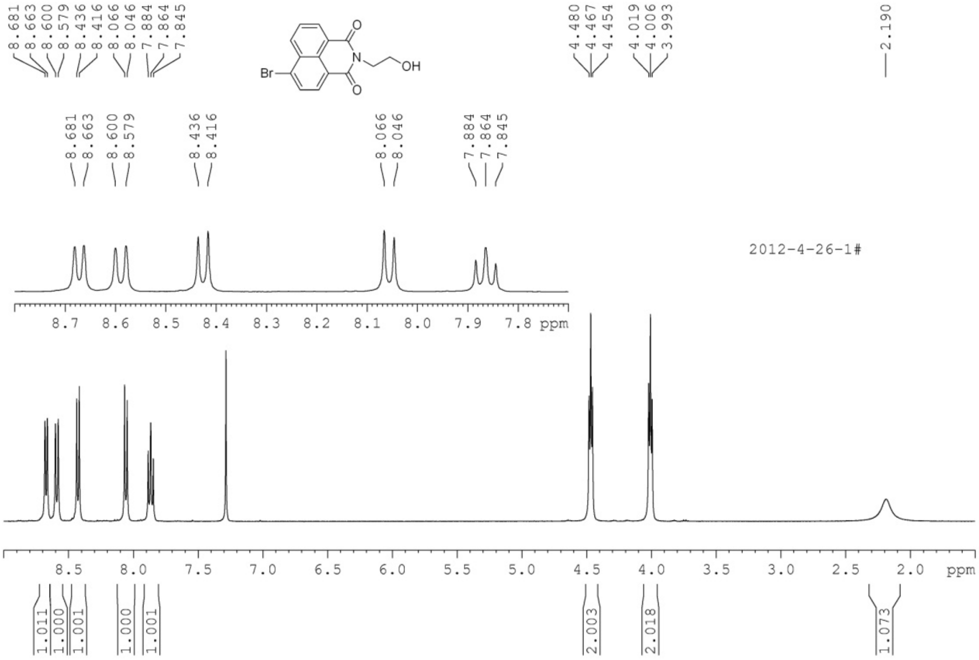
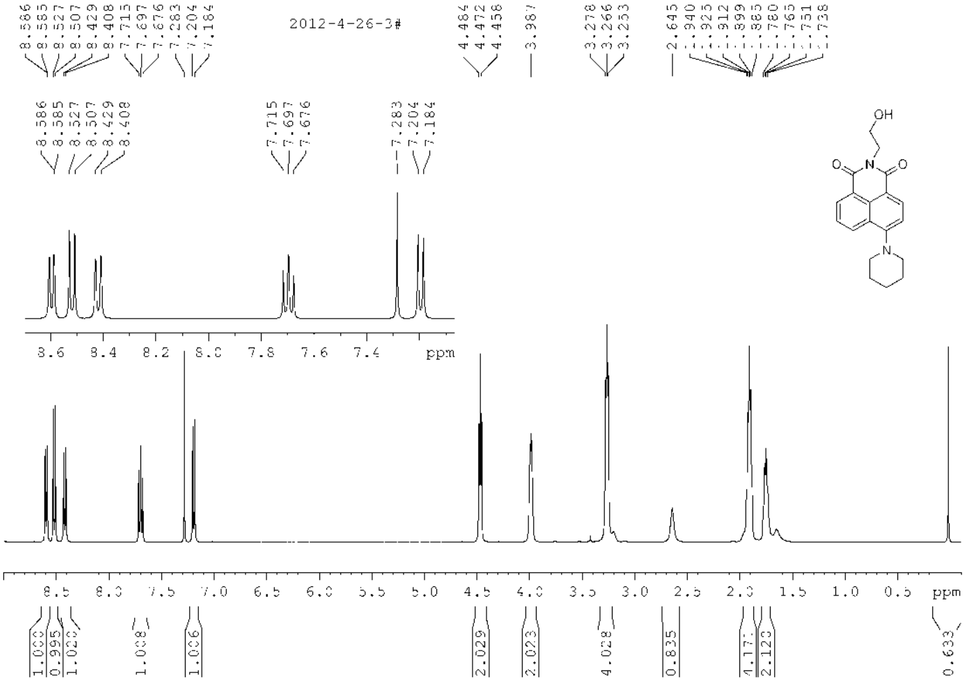
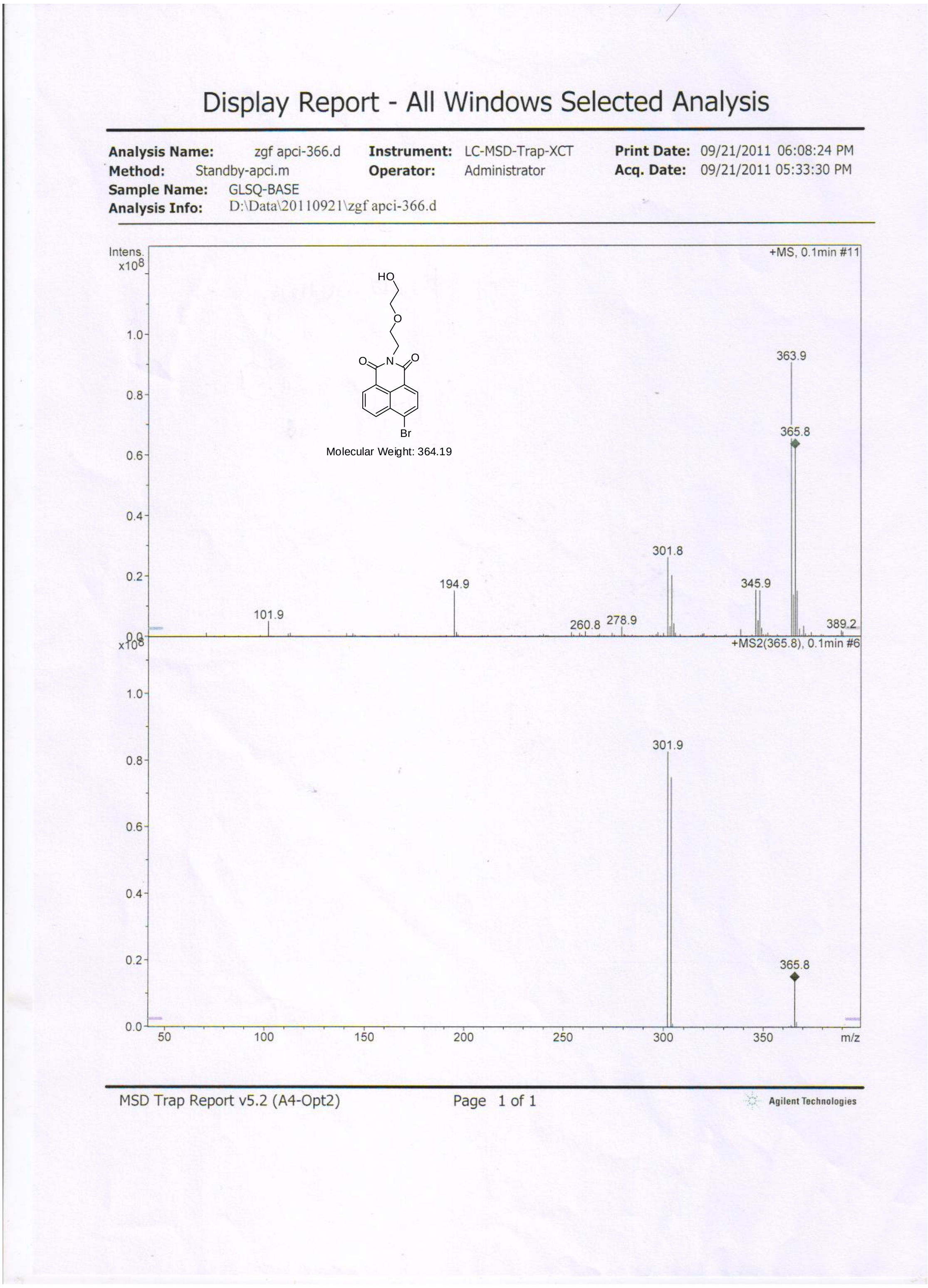


COMPOUND **TPE-PP**



3. MASS SPECTRA.

COMPOUND **2**



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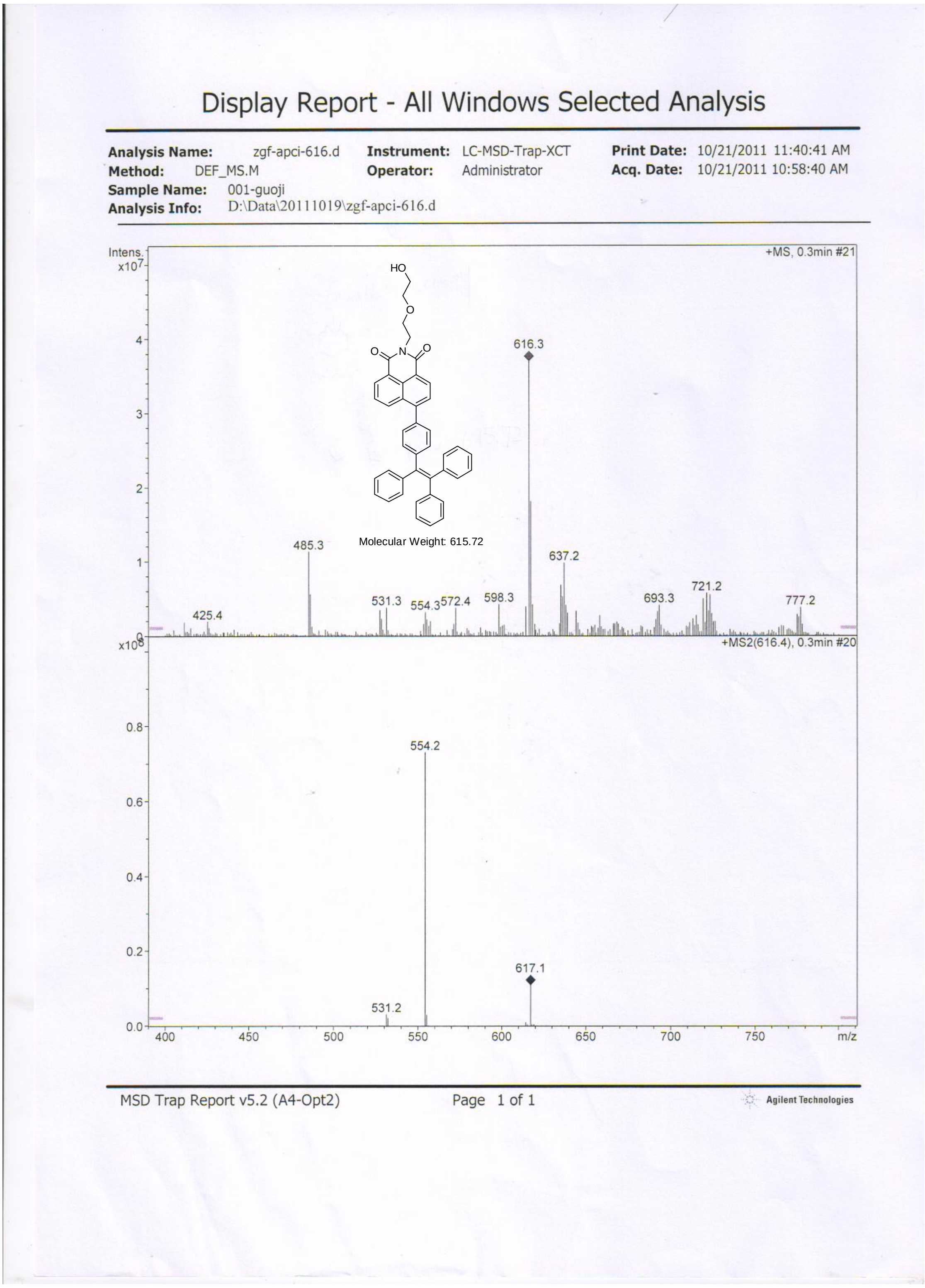
COMPOUND **TPE-NI**



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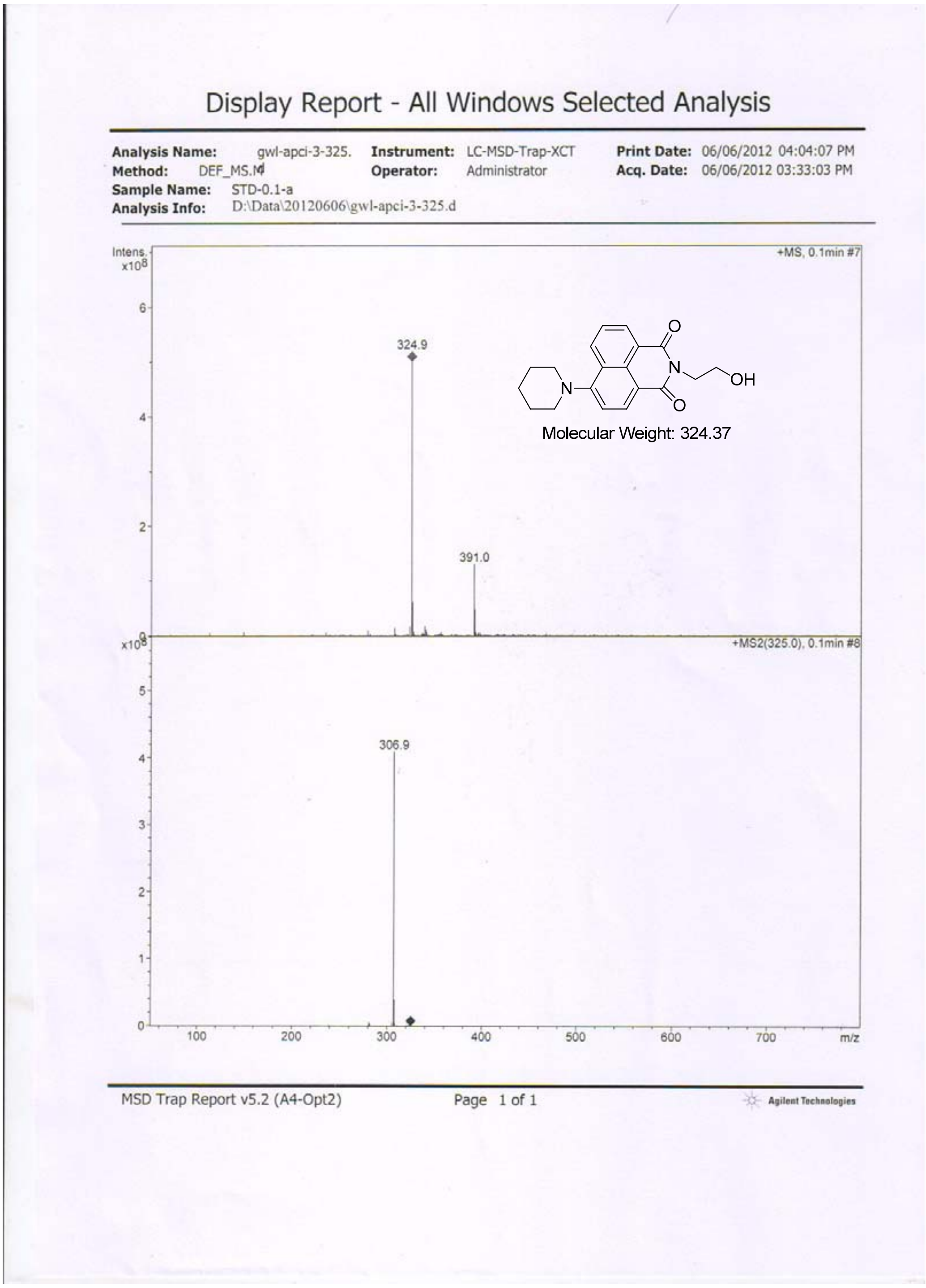
COMPOUND **PP-NI**



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4. UV-VIS ABSORPTION SPECTRA OF TPE-NI.

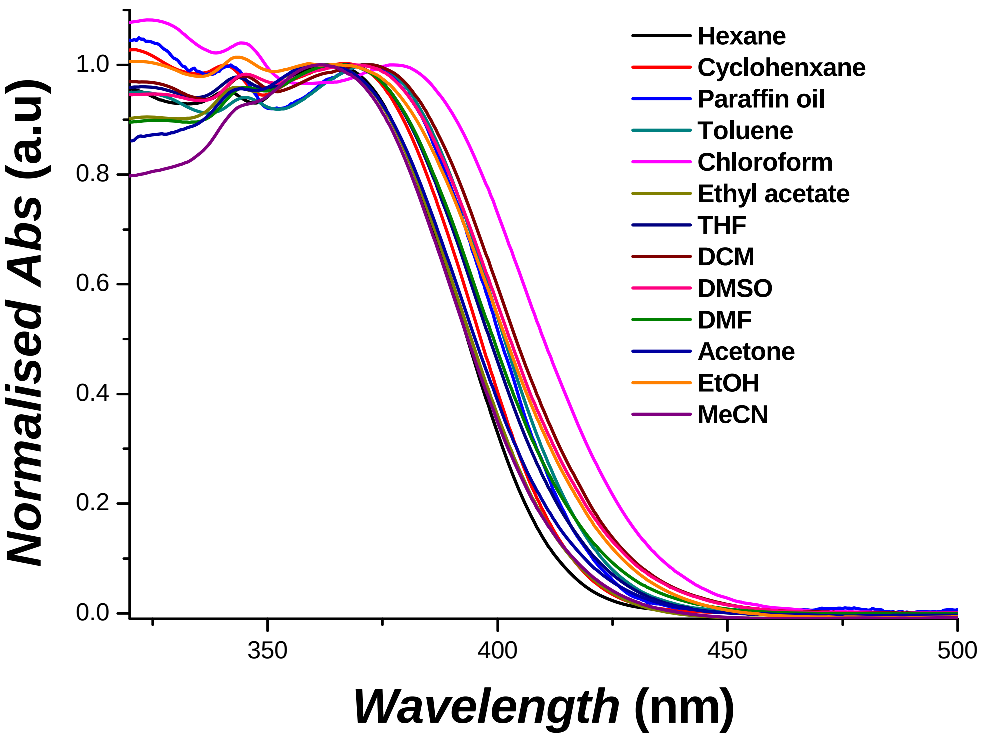

Fig. S1. UV-VIS Absorption in different solvents at concentration = 1 x 10^{-5} M.

5. PL SPECTRA OF TPE-NI IN DIFFERENT THF-WATER SOLVENT MIXTURES (20 % *fw* to 76 % *fw*).

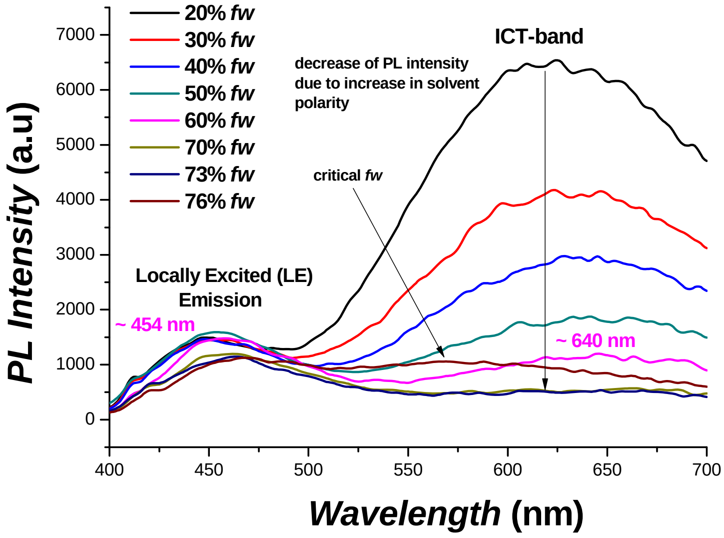

Fig. S5. Emission spectra in THF-water mixtures with different water fractions at concentration = 10^{-5} M, excitation wavelength = 367 nm.

6. PL SPECTRA OF TPE-NI IN DIFFERENT ETHANOL-WATER SOLVENT MIXTURES.

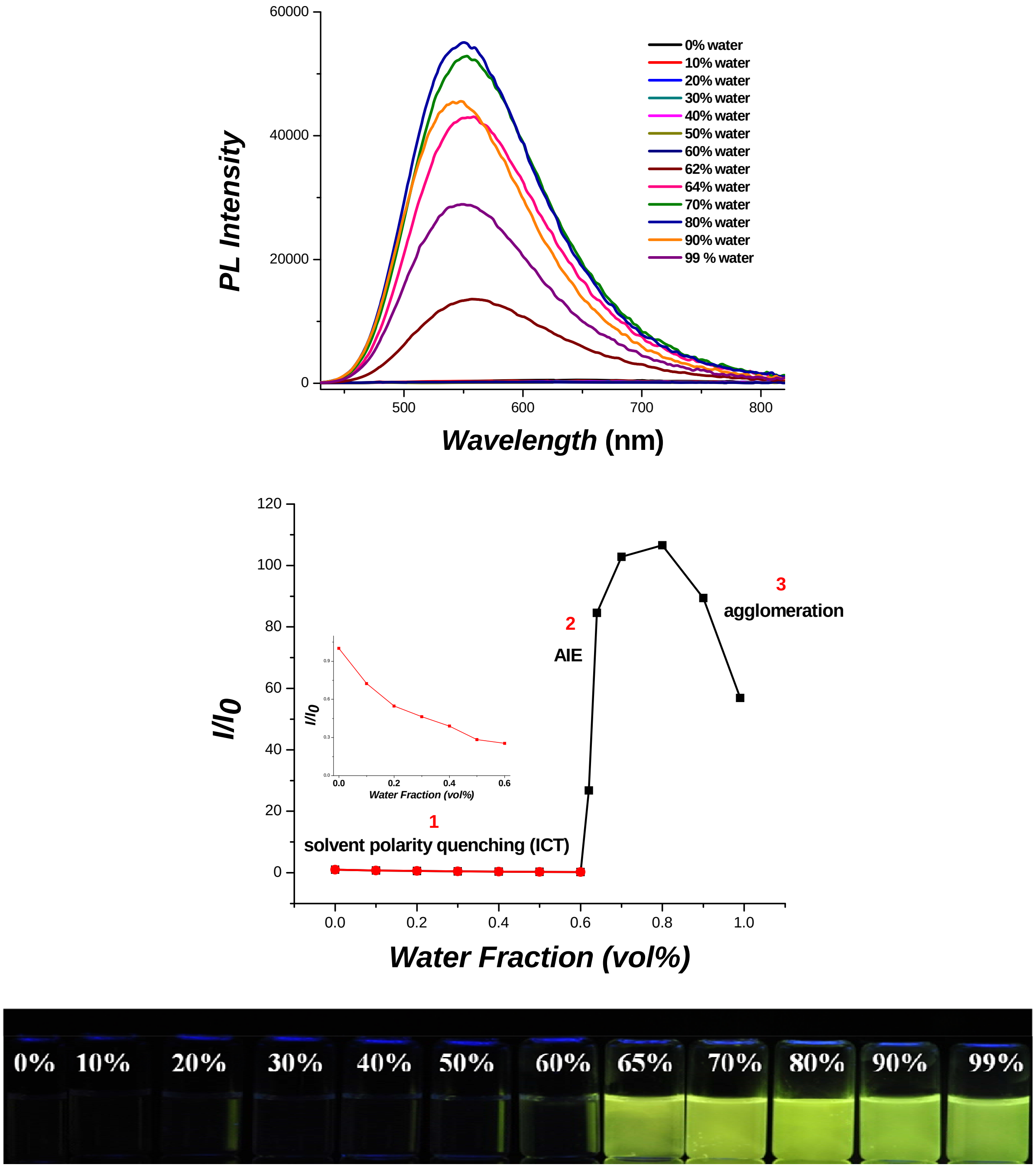

Fig. S7. PL spectra of TPE-NI in different ethanol-water solvent mixtures concentration=1x10^{-5}M, excitation at 420 nm, below the corresponding changes in PL peak intensities (I/I$_0$) (I$_0$ = PL intensity in pure ethanol solution), and at the bottom the corresponding photos over irradiation source (365nm).

7. REVERSIBILITY OF AIE BY THE ADDITION OF THF (0.7 ml) TO A THF-WATER SOLVENT MIXTURE (90 % *fw*).

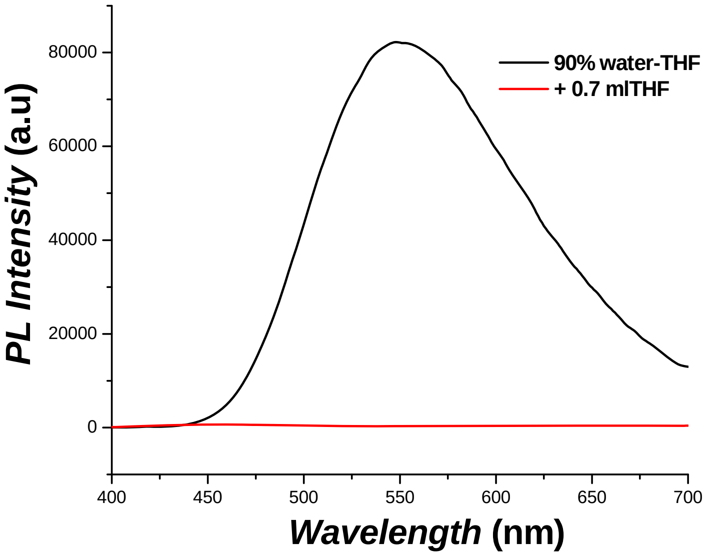

Fig. S6. PL spectra showing the AIE-reversal by the addition of 0.7 ml THF to a 90% water-THF solvent mixture (2 ml) containing TPE-NI (10^{-5}M), excitation = 367 nm).

8. LIPPERT-MATAGA PLOT OF TPE-NI.

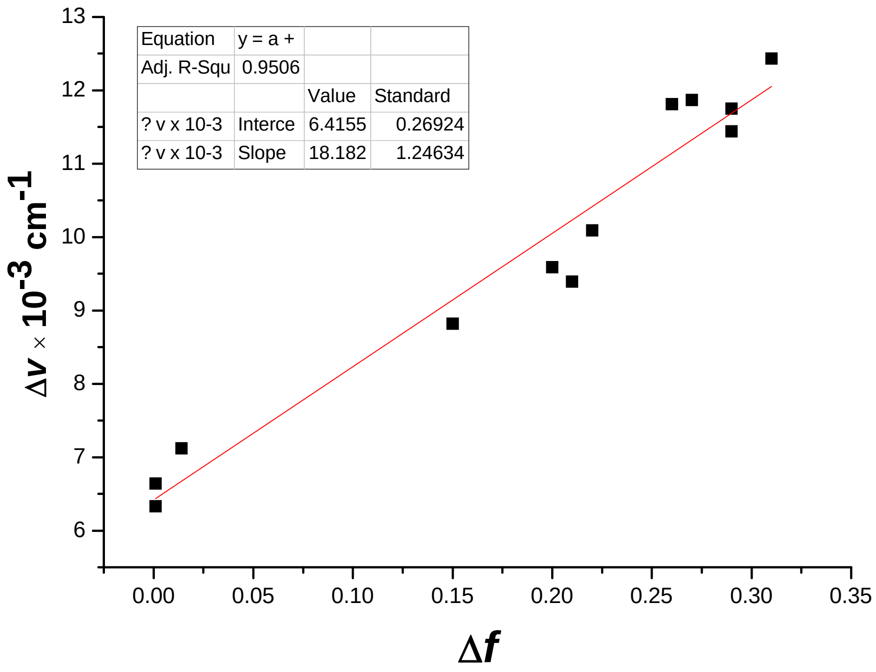

Fig. S2. Stokes Shift (Δv) of TPE-NI as a function of the solvent polarity parameter (Δf).

9. MOLECULAR MODELLING: HOMO AND LUMO LEVELS OF TPE-NI.

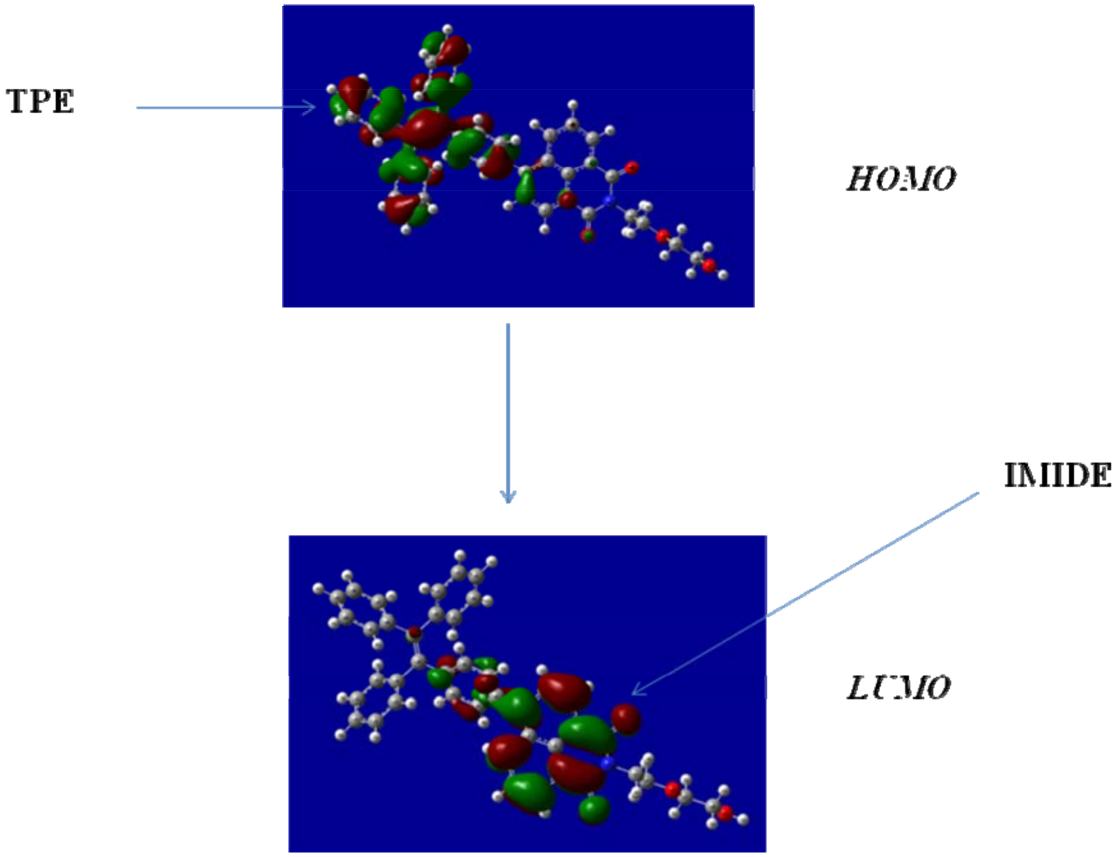

Fig. S3. HOMO-LUMO energy levels of TPE-NI calculated using the B3LYP/6-31G(d) basis set.

10.SEM IMAGE AND FLUORESCENCE IMAGING.

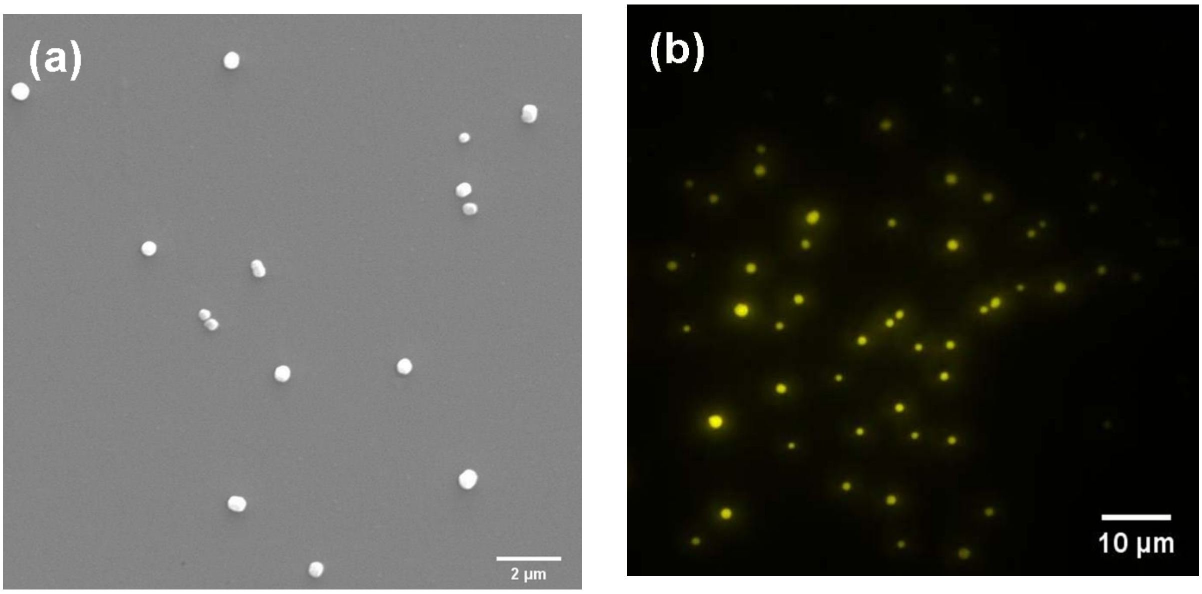

Fig. S8. SEM Image (a) and Fluorescence Imaging (b) of TPE-NI, after evaporation of a 9:1 water-THF solvent mixture, concentration = 10^{-5}M.

11.OPTICAL PROPERTIES OF PP-NI.

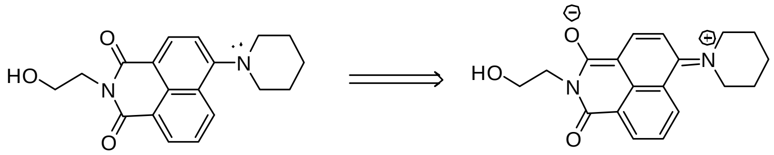

Table S1. Optical Properties.

Solvent	Δf	λ_{max} (abs)	λ_{max} (PL)
hexane	0.001	392	476
toluene	0.014	402	505
ethylacetate	0.20	399	526
DCM	0.22	414	529
acetone	0.29	403	539
ethanol	0.29	406	543
solid state	-	-	545

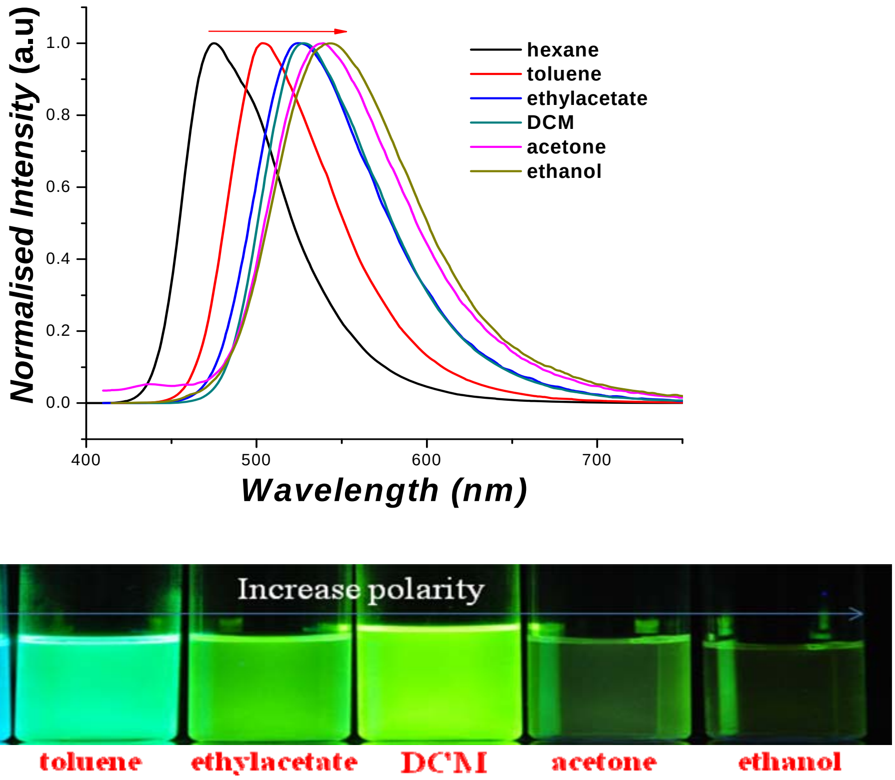

Fig. S4. PL spectra of PP-NI in different solvents and below the corresponding photos, concentration=1x10^{-5}M, PL spectra excitation= λ_{max} (absorption) and photo at irradiation 365 nm.

12. REFERENCES.

1. Tian, H.; Gan, J.; Chen, K.; He, J.; Song, Q. L.; Hou, X. Y., Positive and negative fluorescent imaging induced by naphthalimide polymers, *J. Mater. Chem.*, **2002,** 12, 1262–1267.
2. Aldred, M. P.; Li, C.; Zhang, G.-F.; Gong, W.-L.; Li, A. D. Q.; Dai, Y.; Ma, D.; Zhu, M.-Q., Fluorescence quenching and enhancement of vitrifiable oligofluorenes end-capped with tetraphenylethene, *J. Mater. Chem.*, **2012**, 12, 7515-7528.