Supporting Information

Boron–π–nitrogen-based Conjugated Porous Polymers with Multi-Function

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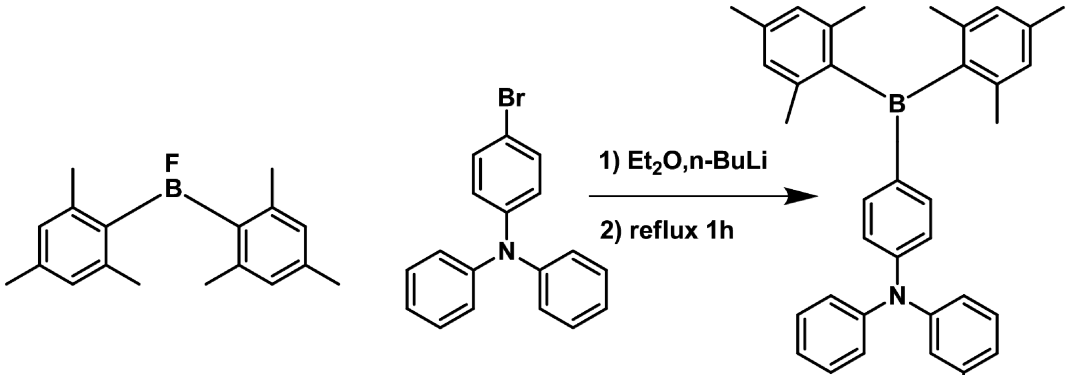
General Methods

All starting materials were purchased from Aladdin and Aldrich. All air-sensitive reactions were carried out under nitrogen atmosphere and performed using Schlenk techniques. All solvents were dried before use. Tetrahydrofuran (THF) was refluxed with sodium. Triethylamine (TEA) and dichloromethane were refluxed with calcium hydroxide. 4-(dimesitylboryl)- N,N-diphenylaniline were synthesized according to the reported procedures. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Mercury Plus 400 (400 MHz for proton) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent in all cases.

Materials synthesis and characterization

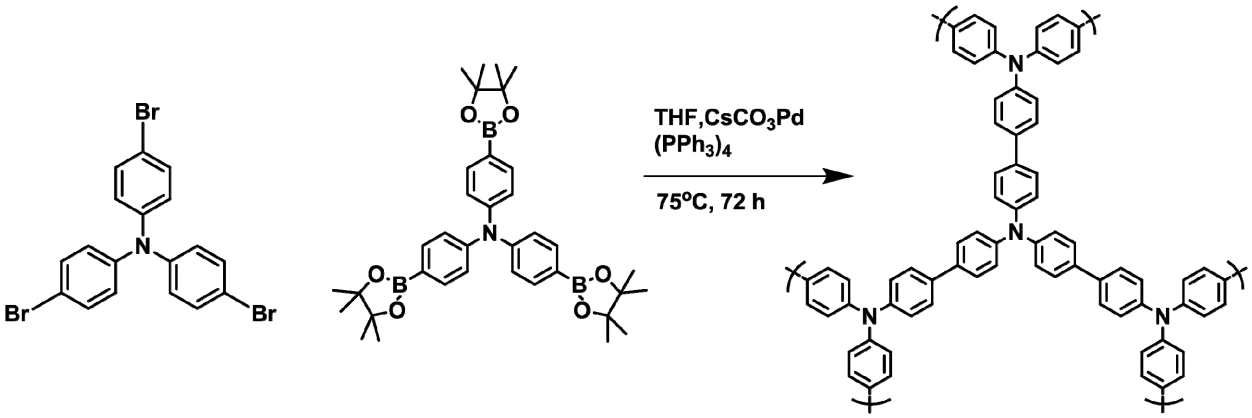
Synthesis of 4-(dimesitylboryl)-N, N-diphenylaniline (B1N1)[1]



To the solution of 4-bromo-N, N-diphenylaniline (0.5 g, 1.54 mmol) in dry Et_2O (30 mL) added n-BuLi (1.62 mmol, 1.6 M) at RT. After 10 min stirring, solution of Mes_2BF (0.83 g, 3.09 mmol) in Et_2O

(5 mL) was added dropwise and reaction mixture was refluxed for 1 h. After cooling to room temperature, reaction was quenched by addition of water (20 mL) and organic phase was separated by extraction. Collected organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Upon addition of acetonitrile to the crude mixture, pale yellow solid precipitated out. It was collected by filtration. Pure product was obtained (0.51 g,75%). 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 (d, J=8.22 Hz, 2H), 7.30-7.267 (m, 4H) 7.15 (d, J=7.64 Hz, 4H), 7.10-7.06 (m, 2H), 6.90 (d, J=8.32 Hz, 2H), 6.79 (s, 4H), 2.28 (s, 6H), 2.05 (s, 12H).

Synthesis of porous polymer NN-ph



4,4,4-(Tri(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))triphenylamine (388.0 mg, 0.62 mmol) and tris(4-bromophenyl)amine (300.0 mg, 0.62 mmol) were dissolved in 35 mL of $CsCO_3$/THF solution. The reaction mixture was degassed for 30 min, tetrakis(triphenylphosphine)palladium was then added to the reaction mixture and heated to 75°C for 72 h under nitrogen atmosphere. The mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed four times with chloroform (3×50 mL), water (3×50 mL), methanol (3×50 mL), and acetone (3×50 mL) to remove any un-reacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 h. The product was then dried under vacuum for 24 h at 60 °C to give grey powder in 83% yield. Elemental analysis calcd for **NN-ph**: C, 96.94; N, 2.34; H, 1.72. Found: C, 95.03; N, 3.15; H, 1.82.

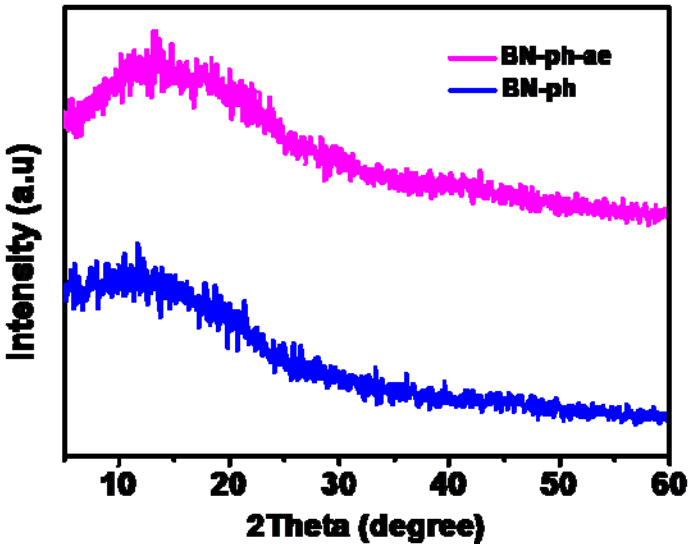


Fig. S1 (a) XRD pattern of **BN-ph** and **BN-ph-ae**

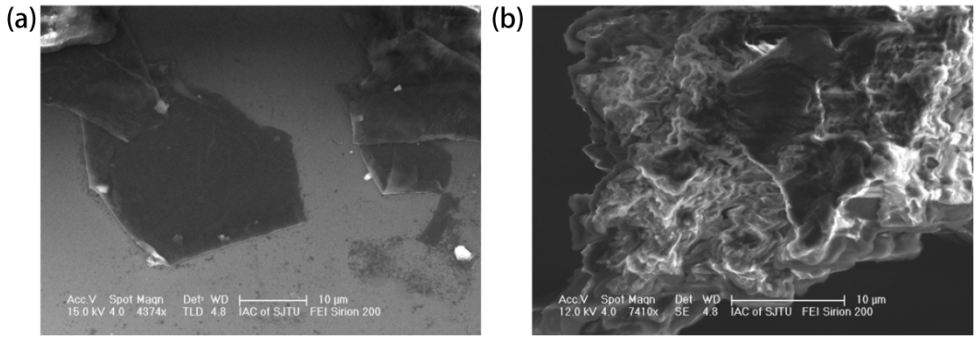


Fig. S2 SEM images of (a) **BN-ph** and (b) **BN-ph-ae**.

Table. S1 Pore structure properties of **BN-ph** and **BN-ph-ae**.

Sample	S_{BET} $(m^2/g)^a$	S_{Lang} $(m^2/g)^b$	S_{micro} $(m^2/g)^c$	V_{micro} $(cm^3/g)^d$	V_{total} $(cm^3/g)^e$	$P_{NL\text{-}DFT}$ $(nm)^f$
BN-ph	1279	2307	884	0.54	0.81	1.54
BN-ph-ae	634	824	498	0.23	0.30	1.61

[a]Surface areas calculated from the N_2 adsorption isotherm using the BET method. [b]The Langmuir surface area calculated from the N_2 adsorption isotherm by application of the Langmuir equation. [c]Micropore surface area calculated from the N_2 adsorption isotherm using the t-plot method. [d]Micropore volume derived using the t-plot method based on the Halsey thickness equation. [e]Total pore volume at P/P_0 =0.99. [f]Pore size calculated from N_2 adsorption isotherms using non-local density functional theory (NL-DFT).

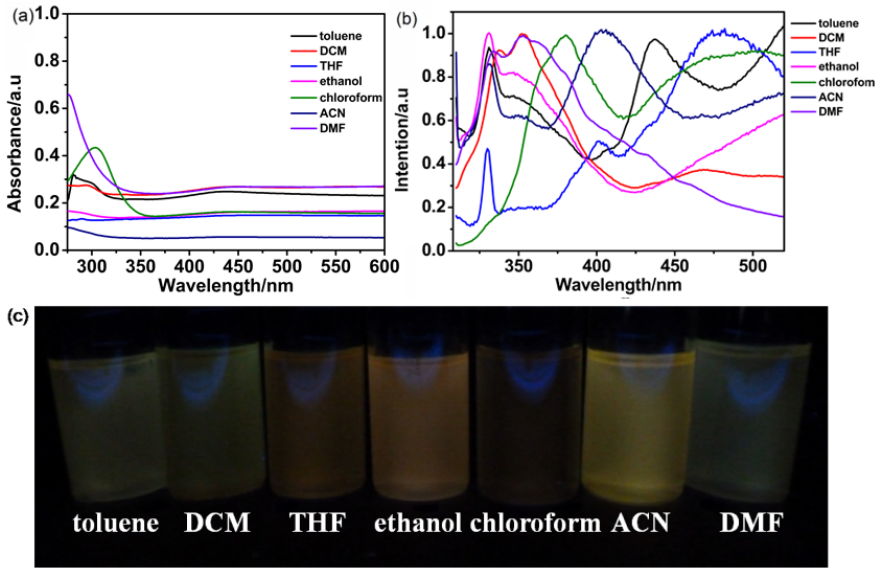


Fig. S3 (a) UV-vis and (b) Normalized fluorensence (λ_{ex} = 300 nm) of **BN-ph-ae**; (c) Luminescence photographs of **BN-ph-ae** in different solvents under UV irradiation (λ_{ex} = 365 nm).

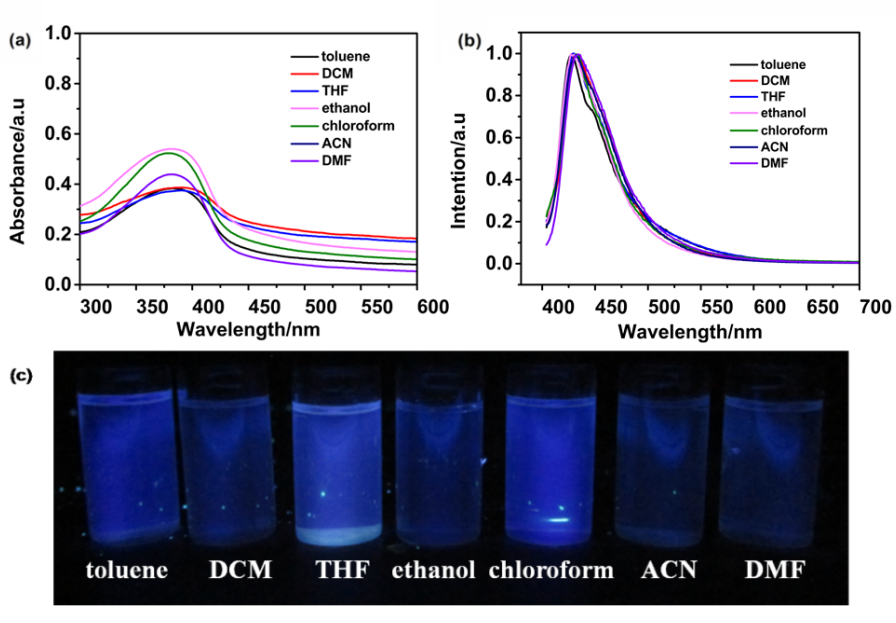


Fig. S4 (a) UV-vis and (b) Normalized fluorescence (λ_{ex} = 386 nm) of **NN-ph**; (c) Luminescence photographs of **NN-ph** in different solvents under UV irradiation (λ_{ex} = 365 nm).

References

1 A. Proń, M. Baumgarten, K. Muellen, *Org. Lett.*, 2010, **12**, 4236.