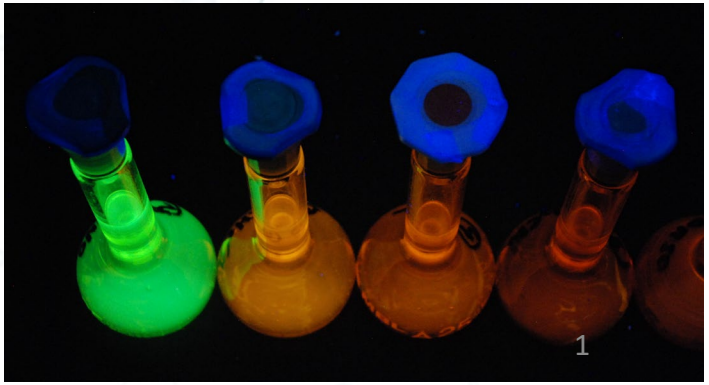
N,N-dimethyl-4-amino-2,1,3-benzothiadiazole: synthesis and luminescent solvatochromism

Valentina Ferraro [1,], Matteo Girotto [1], Marco Bortoluzzi [1]*

[1] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30170 Mestre (VE), Italy. E-mail: valentina.ferraro@unive.it



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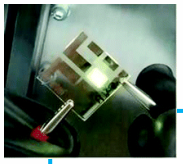

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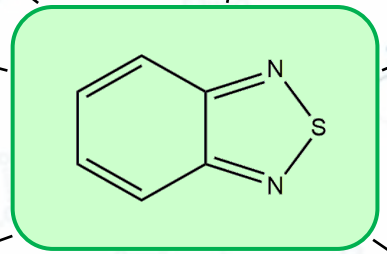

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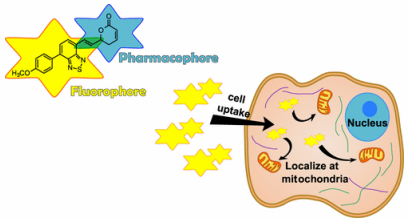

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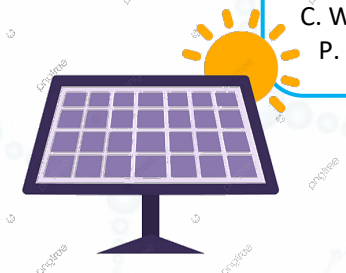
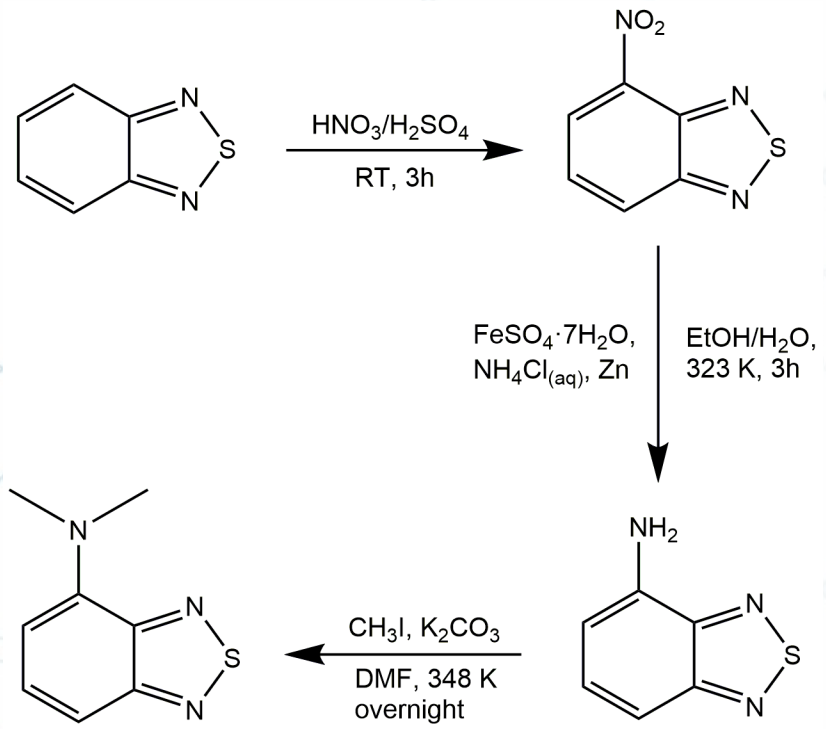


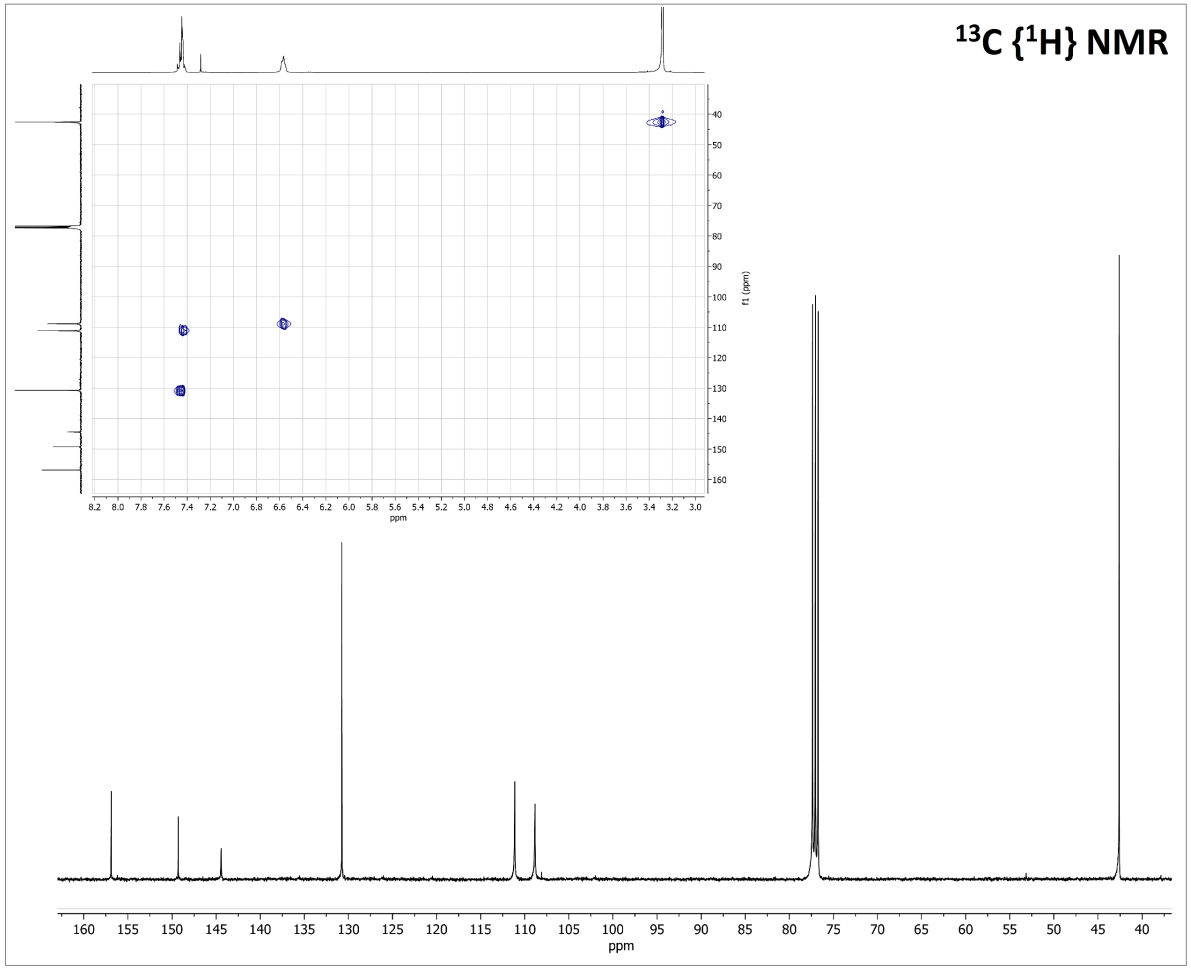
Synthesis



Step 1: **Nitration**

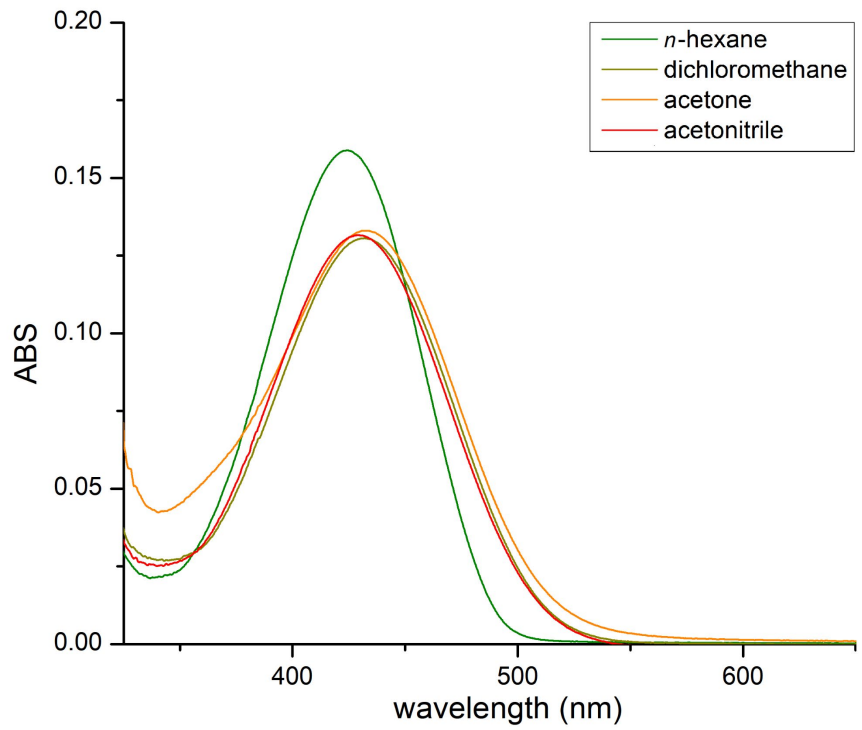
Step 2: **Reduction**

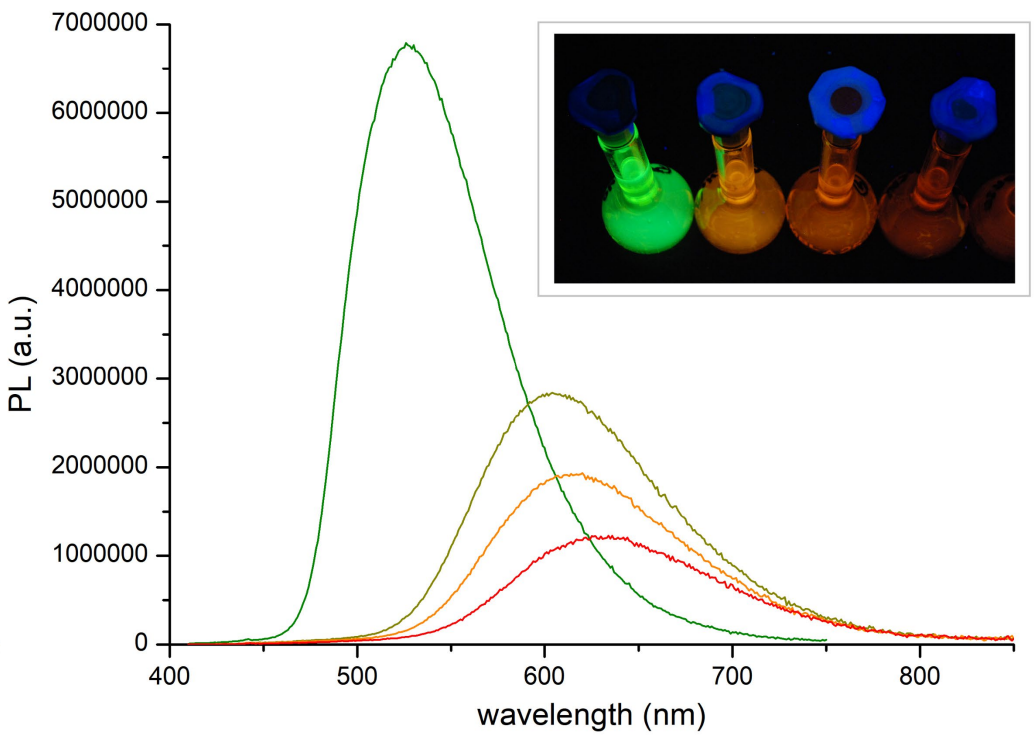
Step 3: **Methylation**



^{1}H NMR spectrum of BTD^{NMe2} in $CDCl_3$ at 298 K. Inset: ^{13}C {^{1}H} NMR and ^{1}H-^{13}C HSQC in $CDCl_3$ at 298 K

Spectroscopic characterization

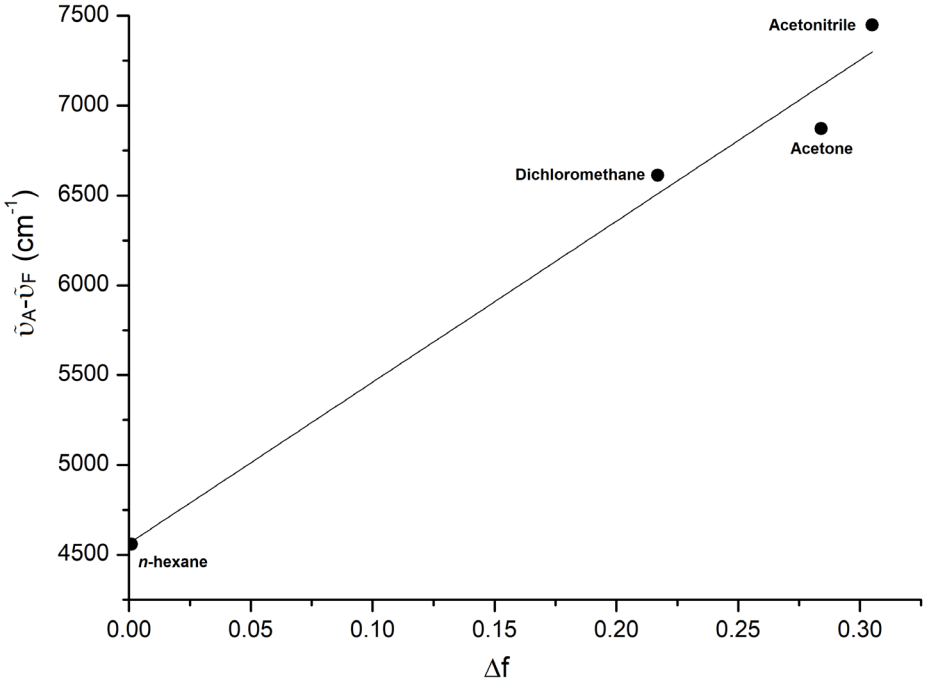


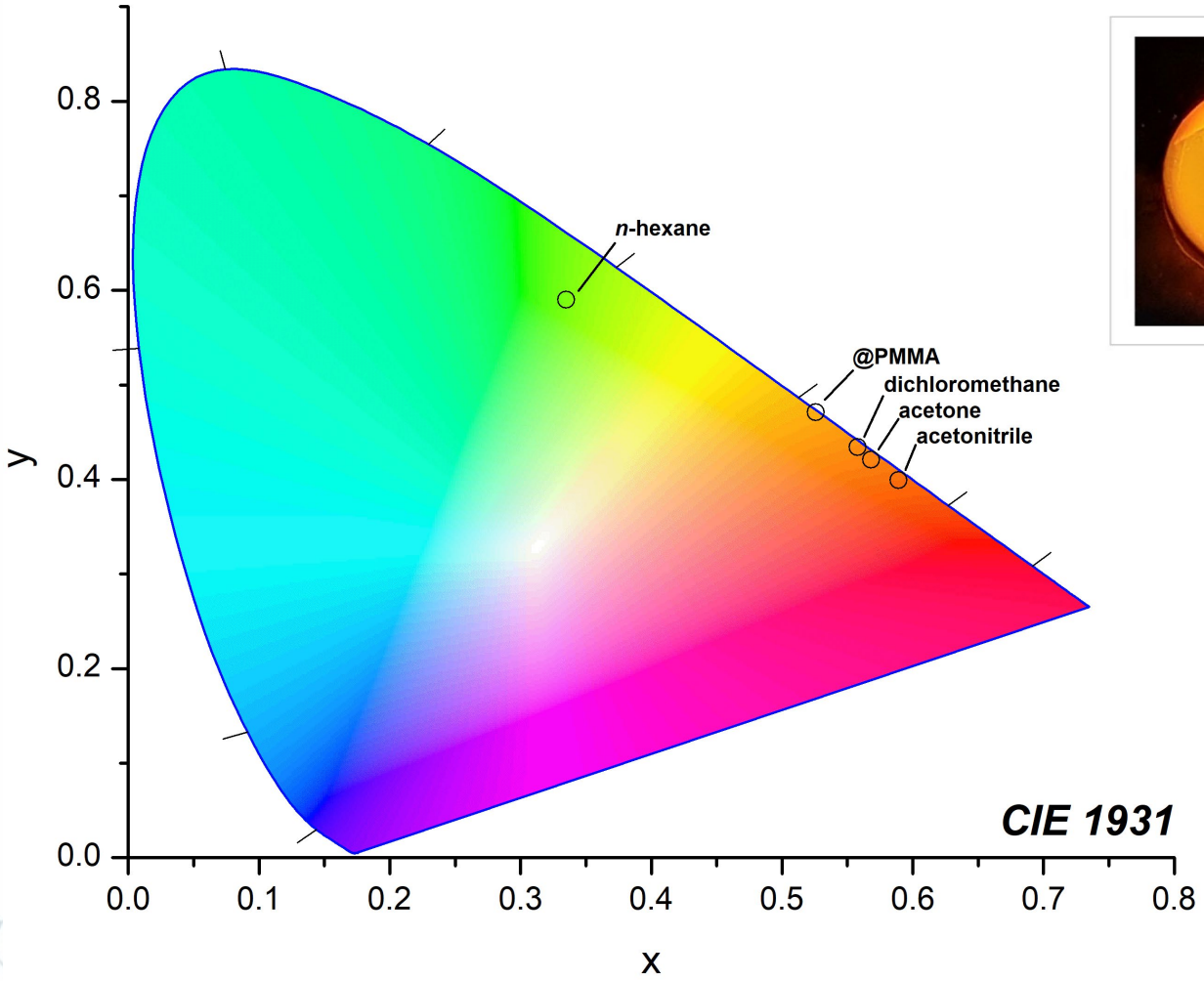


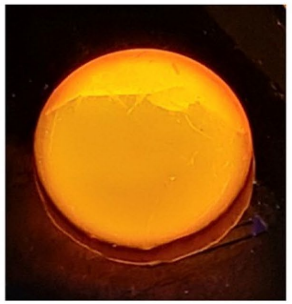
Absorption and emission spectra of $5 \cdot 10^{-5}$ M solutions of BTD^{NMe2} in different solvents recorded at room temperature.
Inset: picture of the solutions under UV light ($\lambda_{excitation}$ = 365 nm).

Solvent	ε	n	ABS max (nm) [a]	PL max (nm) [b]	Stokes shift (cm^{-1})	Φ_F (%) [c]	Orientation Polarizability
n-hexane	1.9	1.375	424	526	4559	52	0.001
Dichloromethane	8.9	1.424	432	604	6613	41	0.217
Acetone	20.7	1.359	433	616	6872	23	0.284
Acetonitrile	37.5	1.479	430	630	7448	16	0.305

[a] 298 K. [b] $\lambda_{excitation}$ = 390 nm, 298 K. [c] Data obtained using a solution of anthracene in ethanol as standard (Φ_F = 27%).

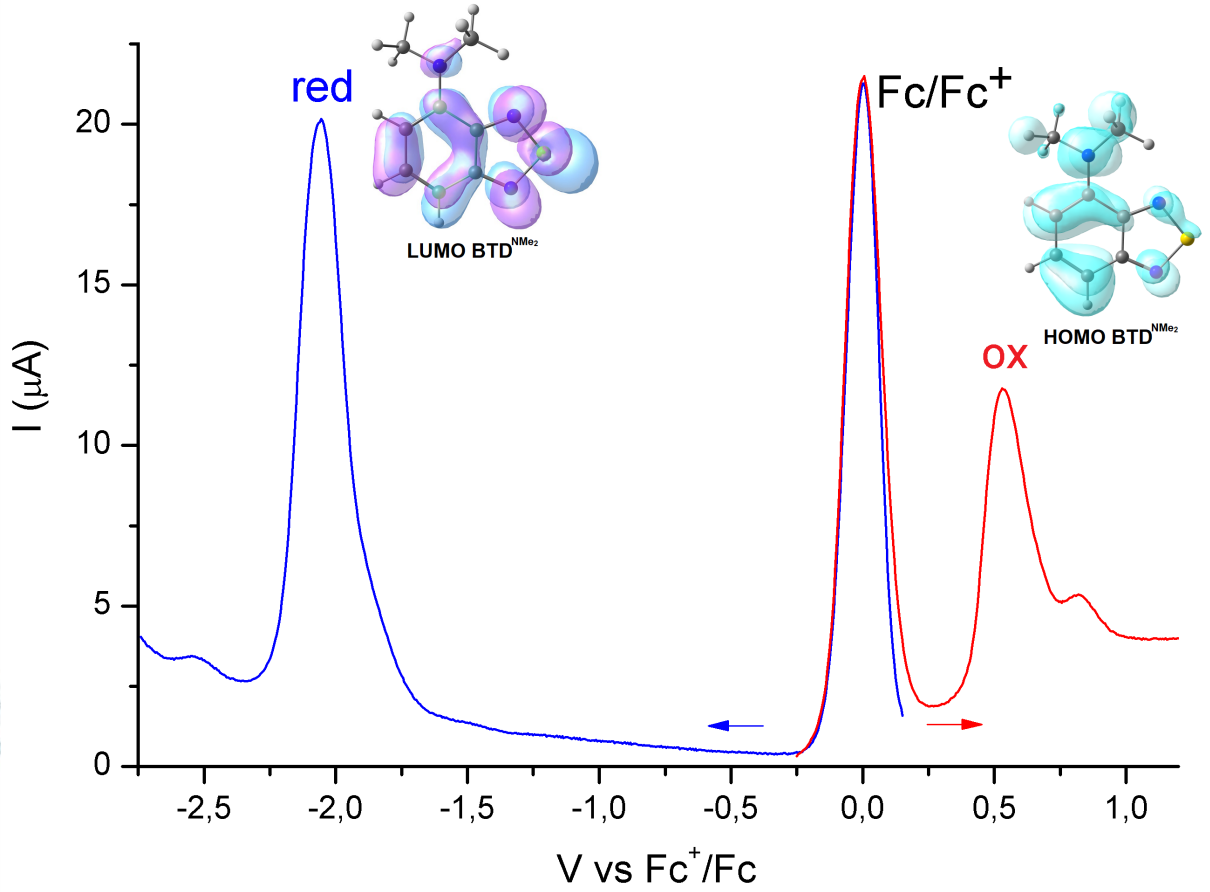






CIE 1931 chromaticity diagram of BTD^{NMe2} in different solvents and in PMMA (***n*-hexane**: x = 0.335, y = 0.590; **dichloromethane**: x = 0.558, y = 0.434; **acetone**: x = 0.561, y = 0.421; **acetonitrile**: x = 0.589 , y = 0.399; **@PMMA**: x = 0.526, y = 0.471). Inset: BTD^{NMe2}@PMMA excited at 365 nm.

DFT calculations and voltammetry



Square wave voltammetry of BTD^{NMe2} ($CH_3CN/LiClO_4$, ferrocene as internal reference, blue line: reduction, red line: oxidation) and frontier molecular orbitals (surface isovalue 0.03 a.u.).

Conclusion

- *N*,*N*-dimethyl-4-amino-2,1,3-benzothiadiazole (BTD^{NMe2}) was prepared from 2,1,3-benzothiadiazole in a three steps synthetic path that involved nitration, subsequent reduction and methylation.
- The compound was fully characterized by means of nuclear magnetic resonance (NMR) and infrared spectroscopy.
- The compound revealed to be highly fluorescent and characterized by a noticeable solvatochromism.
- The emission features, rationalized on the basis of electrochemical measurements and DFT calculations, were maintained once embedded in polymethylmetacrilate.
- The photoluminescence properties exhibited by BTD^{NMe2} make it a suitable candidate for advanced technology applications.