ABSTRACT

The modeling and synthesis of benzotriazole-based small molecules culminating in a donor–π–acceptor chromophore, **BTz-Ph-BIMz**. A concise, stepwise route from a dibromo-diamine precursor delivered intermediates (a–d) and the target (e) in good isolated yields (a: 87%, b: 73%, c: 69%, d: 75%, e: 71%). TLC monitoring and column chromatography afforded single-spot products; UV–Vis and FT-IR spectroscopy verified the intended transformations, with a systematic bathochromic drift of the low-energy band from ~422–445 nm in intermediates to 471 nm for BTz-Ph-BIMz, consistent with progressive π-extension and end-capping by benzimidazole units.

To rationalize the photophysics and evaluate sensing potential, density functional theory calculations were performed at B3LYP and 6-311G(d,p). The optimized ground-state geometry shows a quasi-planar, rod-like π-skeleton with ~30.1 Å end-to-end conjugation and minimal out-of-plane distortion; the phenyl benzimidazole separation is ~5.6 Å. Frontier orbitals reveal a donor (BIMz/phenyl/bridge) acceptor (BTz) distribution with a HOMO–LUMO separation ≈ 3.30 eV, indicating an intramolecular charge-transfer (ICT) character. TD-DFT predicts a bright $S_0 \rightarrow S_1$ transition ($E_x \approx 2.96$ eV, ≈419 nm, f = 1.78, LHE ≈ 0.94); hole–electron/NTO analysis confirms directed ICT. The dipole moment increases strongly from gas to solution (~3.7 D → 11.86 D), explaining the observed solvatochromism. MEP maps localize binding hotspots at hetero-nitrogen sites, PDOS supports D–π–A partitioning, and TDM analysis with an estimated exciton binding energy ~0.34 eV corroborates long-range yet environment-responsive excitation.

Collectively, the synthetic and computational results establish **BTz-Ph-BIMz** as a robust, visible-light absorber with ICT-dominated excited states, accessible N-donor coordination sites, and strong polarity sensitivity—a combination ideally suited to chemosensing. The molecule is expected to show turn-on (CHEF) responses with closed-shell Lewis-acidic cations (e.g., Zn^{2+}/Al^{3+}), turn-off behavior with paramagnetic Cu^{2+}, and pH-dependent spectral shifts upon protonation, enabling ratiometric or intensity-based detection in solution and thin-film platforms. xx

Keywords: benzotriazole, benzimidazole, D–π–A small molecule, DFT/TD-DFT, intramolecular charge transfer, solvatochromism, chemosensor, UV–Vis, FT-IR, transition density matrix.