Supplementary Information (SI) for Journal of Materials Chemistry A.

# Supporting Information

## Molecular Hybridization of Multiple Resonance Cores and Responsive Heterocycles for Versatile Optoelectronic and Sensing Applications

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## S1. Preparation of TPA-doped materials

The host and guest with the corresponding ratio were heated to 150 ℃ in nitrogen atmosphere. After the guests are completely dissolved in the molten hosts, the mixed solution is cooled to room temperature to form the crystalline doped materials. For host-guest doped materials with low molar ratio, the guest materials were dilute with the DCM solution.

## S2. X-ray crystallographic analysis

Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture 4-circle diffractometer using Cu-Kα (λ = 1.54184 Å). The images were processed and corrected for Lorentz polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT) [1] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms "riding" in idealized positions, by full-matrix least squares against $F^2$ of all data, using SHELXL software.[2] Hydrogen atoms were refined with isotropic displacement parameters. Olex2[3] was used as a graphical user interface and for the preparation of the CIF files. Crystal data and experimental details are listed in Table S1.

**Table S1** Crystal data and structure refinement for **BNNS-OH** and **BNNO-OH**.

| Identification code | **BNNS-OH** | **BNNO-OH** |
|---|---|---|
| CCDC Deposit number | 2527126 | 2527127 |
| Experimental formula | $C_{54.25}H_{45.25}BN_4OS$ | $C_{49}H_{33}BN_4O_2$ |
| Formula weight | 812.06 | 720.60 |
| Temperature/K | 100.03(18) | 100.01(11) |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $Pc$ |
| $a$/Å | 13.9174(3) | 9.6447(3) |
| $b$/Å | 9.7086(2) | 13.6453(3) |
| $c$/Å | 31.7165(6) | 32.5772(9) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 97.4722(19) | 95.217(2) |
| $\gamma$/° | 90 | 90 |
| Volume/Å$^3$ | 4249.09(15) | 4269.6(2) |
| Z | 4 | 4 |
| $\rho_{calc}$/g·cm$^{-3}$ | 1.269 | 1.121 |
| $\mu$/mm$^{-1}$ | 1.027 | 0.540 |
| F(000) | 1657 | 1487 |
| Crystal size/mm$^3$ | 0.10×0.08×0.06 | 0.10×0.08×0.06 |
| Radiation | Cu $K_\alpha$ (λ = 1.54184 Å) | Cu $K_\alpha$ (λ = 1.54184 Å) |
| $2\theta$ range for data collection/° | 2.810 to 77.330 | 2.724 to 77.242 |
| Index ranges | $-16 \leq h \leq 17, -11 \leq k \leq 11, -40 \leq l \leq 38$ | $-12 \leq h \leq 11, -8 \leq k \leq 17, -40 \leq l \leq 40$ |
| Reflections collected | 41042 | 32629 |
| Independent reflections | 8527[$R_{int}$ = 0.0290] | 13654[$R_{int}$ = 0.0320] |
| Data/restraints/parameters | 8527/307/575 | 13654/26/1035 |

| | | |
|---|---|---|
| Goodness-of-fit on $F^2$ | 1.052 | 1.074 |
| Final $R$ indexes [I >= 2σ (I)] | $R_1 = 0.0408$, $wR_2 = 0.1105$ | $R_1 = 0.0511$, $wR_2 = 0.1394$ |
| Final $R$ indexes [all data] | $R_1 = 0.0503$, $wR_2 = 0.1164$ | $R_1 = 0.0538$, $wR_2 = 0.1415$ |
| Largest diff. peak/hole/e $Å^{-3}$ | 0.183/-0.211 | 0.512/-0.229 |

## S3. Theoretical calculations

All quantum chemical calculations were performed using Gaussian 16[4]. Ground-state ($S_0$) geometries were fully optimized using Density Functional Theory at the M06-2X/6-31G(d) level of theory, with solvent effects incorporated via the SMD solvation model using toluene as the solvent. Excited-state calculations were carried out using time-dependent DFT (TD-DFT) at the same level of theory, where the lowest five singlet excited states were considered (TD, nstates = 5). The first singlet excited state ($S_1$) geometries were optimized under these conditions, and vertical excitation energies were obtained from single-point TD-DFT calculations at the optimized geometries. Triplet-state ($T_1$) geometries were optimized using unrestricted DFT at the M06-2X/6-31G(d) level with the SMD solvation model (toluene). All calculations were performed without symmetry constraints using the geom=connectivity specification, and default convergence criteria as implemented in Gaussian 16 were employed throughout. Electron-hole analysis is conducted using Multiwfn software [5].

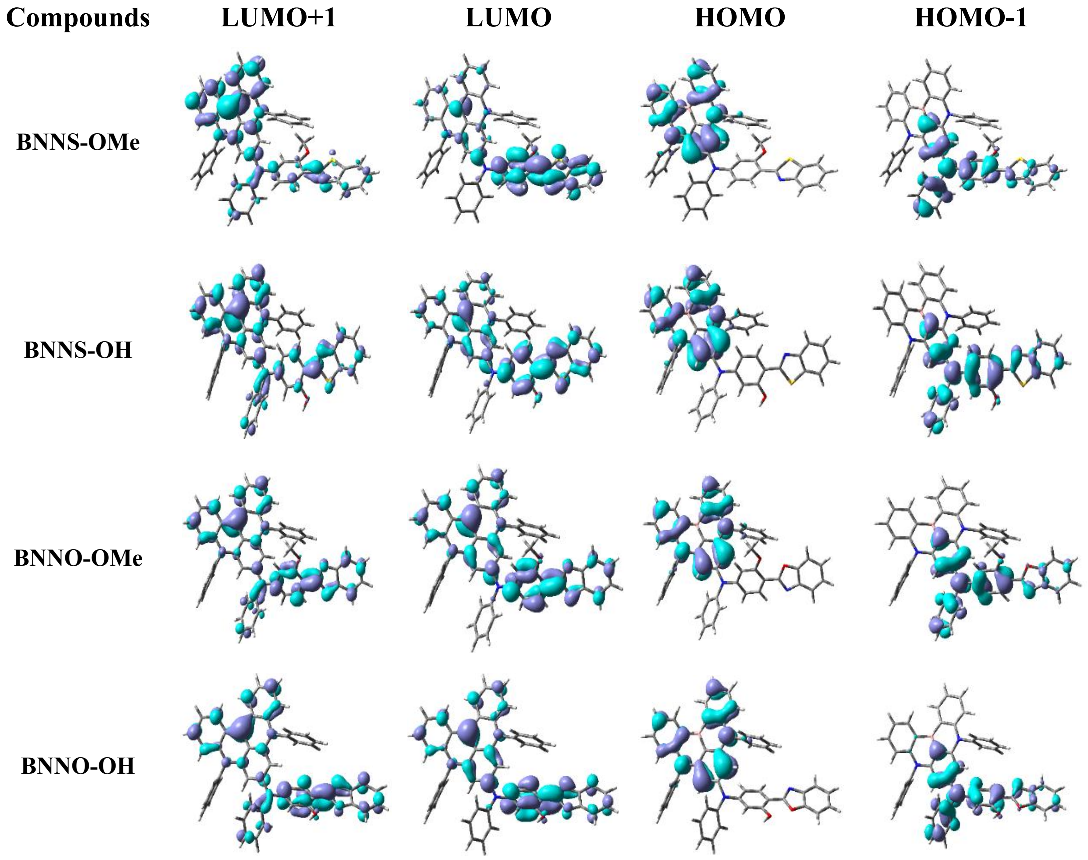


**Figure S1.** Plots of frontier orbitals of target compounds studied in this work.

**Table S2** Vertical transitions in toluene from TD-DFT calculation for **BNNS-OMe**.

| Compound | Spin State | Transition Configuration | Excitation Energy [nm(eV)] | Oscillator Strength |
|---|---|---|---|---|
| **BNNS-OMe** | $S_1$ | HOMO-1 → LUMO (8%) | 351.13 (3.53) | 0.1959 |
| | | HOMO → LUMO (37%) | | |
| | | HOMO → LUMO+1 (50%) | | |
| | $S_2$ | HOMO-1 → LUMO (81%) | 347.60 (3.57) | 1.3534 |
| | | HOMO → LUMO+1 (2%) | | |
| | | HOMO → LUMO+1 (6%) | | |
| | $S_3$ | HOMO-3 → LUMO (4%) | 304.29 (4.07) | 0.3935 |
| | | HOMO-2 → LUMO (3%) | | |
| | | HOMO-1 → LUMO+1 (70%) | | |
| | | HOMO-1 → LUMO+2 (7%) | | |
| | | HOMO-1 → LUMO+7 (3%) | | |
| | $S_4$ | HOMO → LUMO (39%) | 294.17 (4.21) | 0.0614 |
| | | HOMO → LUMO+1 (30%) | | |
| | | HOMO → LUMO+2 (14%) | | |
| | | HOMO → LUMO+10 (3%) | | |
| | $S_5$ | HOMO-3 → LUMO+1 (2%) | 279.31 (4.44) | 0.0059 |
| | | HOMO-2 → LUMO (24%) | | |
| | | HOMO-2 → LUMO+1 (51%) | | |
| | | HOMO-1 → LUMO+2 (4%) | | |
| | | HOMO → LUMO+4 (2%) | | |
| | | HOMO → LUMO+11 (4%) | | |

**Table S3** Vertical transitions in toluene from TD-DFT calculation for **BNNS-OH**.

| Compound | Spin State | Transition Configuration | Excitation Energy [nm(eV)] | Oscillator Strength |
|---|---|---|---|---|
| **BNNS-OH** | $S_1$ | HOMO-1 → LUMO (3%) | 352.02 (3.52) | 0.2619 |
| | | HOMO → LUMO (49%) | | |
| | | HOMO → LUMO+1 (42%) | | |
| | $S_2$ | HOMO-1 → LUMO (83%) | 344.04 (3.60) | 1.4900 |
| | | HOMO-1 → LUMO+1 (3%) | | |
| | | HOMO → LUMO+1 (4%) | | |
| | $S_3$ | HOMO-3 → LUMO (4%) | 302.52 (4.10) | 0.4140 |
| | | HOMO-2 → LUMO (3%) | | |
| | | HOMO-1 → LUMO (2%) | | |
| | | HOMO-1 → LUMO+1 (66%) | | |
| | | HOMO-1 → LUMO+2 (9%) | | |
| | | HOMO-1 → LUMO+7 (3%) | | |
| | $S_4$ | HOMO → LUMO (24%) | 289.63 (4.28) | 0.0112 |
| | | HOMO → LUMO+1 (30%) | | |
| | | HOMO → LUMO+2 (27%) | | |

| | | | | |
|---|---|---|---|---|
| | | HOMO → LUMO+10 (5%) | | |
| | $S_5$ | HOMO-2 → LUMO (33%) | 280.03 (4.43) | 0.0049 |
| | | HOMO-2 → LUMO+1 (43%) | | |
| | | HOMO-1 → LUMO+2 (4%) | | |
| | | HOMO → LUMO+5 (2%) | | |
| | | HOMO → LUMO+12 (4%) | | |

**Table S4** Vertical transitions in toluene from TD-DFT calculation for **BNNO-OMe**.

| Compound | Spin State | Transition Configuration | Excitation Energy [nm(eV)] | Oscillator Strength |
|---|---|---|---|---|
| **BNNO-OMe** | $S_1$ | HOMO → LUMO (64%) | 350.92 (3.53) | 0.3366 |
| | | HOMO → LUMO+1 (31%) | | |
| | $S_2$ | HOMO-1 → LUMO (82%) | 338.98 (3.66) | 1.1720 |
| | | HOMO-1 → LUMO+1 (6%) | | |
| | $S_3$ | HOMO-3 → LUMO (4%) | 301.90 (4.11) | 0.4148 |
| | | HOMO-2 → LUMO (4%) | | |
| | | HOMO-1 → LUMO (4%) | | |
| | | HOMO-1 → LUMO+1 (66%) | | |
| | | HOMO-1 → LUMO+2 (7%) | | |
| | | HOMO-1 → LUMO+7 (3%) | | |
| | $S_4$ | HOMO → LUMO (16%) | 290.47 (4.27) | 0.0496 |
| | | HOMO → LUMO+1 (39%) | | |
| | | HOMO → LUMO+2 (25%) | | |
| | | HOMO → LUMO+3 (2%) | | |
| | | HOMO → LUMO+10 (4%) | | |
| | $S_5$ | HOMO-3 → LUMO (2%) | 279.31 (4.44) | 0.0075 |
| | | HOMO-2 → LUMO (42%) | | |
| | | HOMO-2 → LUMO+1 (32%) | | |
| | | HOMO-1 → LUMO+2 (4%) | | |
| | | HOMO → LUMO+4 (2%) | | |
| | | HOMO → LUMO+10 (4%) | | |

**Table S5** Vertical transitions in toluene from TD-DFT calculation for **BNNO-OH**.

| Compound | Spin State | Transition Configuration | Excitation Energy [nm(eV)] | Oscillator Strength |
|---|---|---|---|---|
| **BNNO-OH** | $S_1$ | HOMO → LUMO (65%) | 353.02 (3.51) | 0.2692 |
| | | HOMO → LUMO+1 (28%) | | |
| | $S_2$ | HOMO-1 → LUMO (80%) | 337.25 (3.68) | 1.2679 |
| | | HOMO-1 → LUMO+1 (6%) | | |
| | | HOMO → LUMO+1 (3%) | | |
| | $S_3$ | HOMO-3 → LUMO (4%) | 300.15 (4.13) | 0.4677 |
| | | HOMO-2 → LUMO (4%) | | |
| | | HOMO-1 → LUMO (5%) | | |
| | | HOMO-1 → LUMO+1 (61%) | | |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  | HOMO-1 → LUMO+2 (9%) |  |  |
|  |  | HOMO-1 → LUMO+7 (3%) |  |  |
|  |  | HOMO → LUMO+1 (3%) |  |  |
|  | $S_4$ | HOMO-1 → LUMO+1 (3%) | 290.44 (4.27) | 0.0259 |
|  |  | HOMO → LUMO (14%) |  |  |
|  |  | HOMO → LUMO+1 (33%) |  |  |
|  |  | HOMO → LUMO+2 (31%) |  |  |
|  |  | HOMO → LUMO+10 (4%) |  |  |
|  | $S_5$ | HOMO-2 → LUMO (45%) | 279.98 (4.43) | 0.0064 |
|  |  | HOMO-2 → LUMO+1 (31%) |  |  |
|  |  | HOMO-1 → LUMO+2 (4%) |  |  |
|  |  | HOMO → LUMO+4 (2%) |  |  |
|  |  | HOMO → LUMO+11 (3%) |  |  |

# S4. Excited-state proton-transfer analysis

## S4.1 Computational methods

Ground-state hydrogen-bonded enol conformers were optimized at the M06-2X/6-31G(d) level with the SMD solvation model for toluene, consistent with the ground-state optimization protocol used in the manuscript. Excited-state geometry optimizations, relaxed S1 proton-transfer scans, unconstrained S1-keto* optimizations, and TD-DFT/NTO analyses were performed using TDA-CAM-B3LYP/def2-SVP with RIJCOSX/def2/J acceleration and the SMD solvation model for toluene in ORCA[6]. Five singlet roots were included, and the first excited singlet state was followed during the S1 optimizations and scans. Natural transition orbital (NTO) analyses were performed based on the TD-DFT results. The NTO cube files were generated using Multiwfn and visualized with VMD[7].

The proton-transfer coordinate was defined as (q = r(O-H) - r(N-H)), where negative (q) values correspond to the enol* region and positive (q) values correspond to the keto-like region.

### S4.2 Hydrogen-bonded enol conformers

Since ESIPT requires an intramolecular O-H···N preorganization, hydrogen-bonded enol conformers were constructed and optimized for **BNNO-OH** and **BNNS-OH**. For **BNNO-OH**, the hydrogen-bonded enol conformer is lower in energy than the previously considered non-hydrogen-bonded conformer by ca. 9.2 kcal mol$^{-1}$, indicating that the O-H···N preorganized conformer is energetically accessible and more suitable for evaluating the ESIPT pathway.

**Table S6**. Key optimized geometric and energetic parameters for the ESIPT analysis.

| **Molecule** | **Geometry** | **r(O-H) / Å** | **r(N-H) / Å** | **r(O···N) / Å** | **q / Å** | **Relative S1 energy / kcal mol$^{-1}$** |
|---|---|---|---|---|---|---|
| **BNNO-OH** | S0 hydrogen-bonded enol | 0.985 | 1.814 | 2.683 | -0.828 | |
| **BNNO-OH** | S1-enol* | 0.992 | 1.731 | 2.622 | -0.739 | 0.00 |
| **BNNO-OH** | S1-keto* | 1.724 | 1.048 | 2.553 | 0.676 | 6.77 |
| **BNNS-OH** | S0 hydrogen-bonded enol | 0.988 | 1.769 | 2.646 | -0.781 | |
| **BNNS-OH** | S1-enol* | 1.006 | 1.648 | 2.570 | -0.642 | 0.00 |
| **BNNS-OH** | S1-keto* | 1.643 | 1.058 | 2.537 | 0.585 | 4.74 |

Note: For enol structures, r(N-H) denotes the nonbonded H···N distance. For keto* structures, r(O-H) denotes the nonbonded O···H distance and r(N-H) denotes the formed N-H bond. Relative S1 energies are referenced to the corresponding optimized S1-enol* minima.

### S4.3 S1-enol* and S1-keto* optimized geometries

Starting from the optimized hydrogen-bonded enol conformers, S1-enol* geometry optimizations were performed. The optimized S1-enol* structures retain the intramolecular O-H···N preorganization. The O···N distance slightly decreases from 2.683 Å in S0-enol to 2.622 Å in S1-enol* for **BNNO-OH**, and from 2.646 Å to 2.570 A for **BNNS-OH**, indicating that excited-state relaxation does not disrupt the proton-transfer-ready geometry.

To verify whether the product-side shallow basins in the relaxed S1 proton-transfer scans correspond to true keto*-like minima, unconstrained S1-keto* optimizations were performed using product-side scan structures as initial geometries. For both **BNNO-OH** and **BNNS-OH**, stable keto*-like minima with a formed N-H bond were located. These keto* minima remain higher in energy than the corresponding S1-enol* minima by 6.77 kcal mol$^{-1}$ for **BNNO-OH** and 4.74 kcal mol$^{-1}$ for **BNNS-OH**.

### S4.4 Relaxed S1 proton-transfer PES scans

Relaxed S1 proton-transfer potential-energy surface scans were performed along q = r(O-H) - r(N-H). The scans reveal shallow product-side basins rather than deeply stabilized keto* wells.

**Figure S2**. Relaxed S1 proton-transfer potential-energy surface scans of **BNNO-OH** and **BNNS-OH** along the coordinate q = r(O-H) - r(N-H), calculated at the TDA-CAM-B3LYP/def2-SVP/SMD(toluene) level. The relative energies are referenced to the corresponding optimized S1-enol* minima. Stars denote the unconstrained optimized S1-enol* minima, and diamonds denote the unconstrained optimized S1-keto* minima. Although keto-like minima can be located for both molecules, they remain higher in energy than the corresponding enol* minima, indicating that the proton-transfer channel is energetically attenuated.

**Table S7**. Numerical data for the relaxed S1 proton-transfer scans.

| Molecule | Step | r(O-H) / Å | r(N-H) / Å | q / Å | Relative S1 energy / kcal $mol^{-1}$ |
|---|---|---|---|---|---|
| **BNNO-OH** | 1 | 0.990 | 1.730 | -0.740 | 0.00 |
| **BNNO-OH** | 2 | 1.041 | 1.665 | -0.625 | 0.85 |
| **BNNO-OH** | 3 | 1.092 | 1.601 | -0.509 | 2.95 |
| **BNNO-OH** | 4 | 1.143 | 1.536 | -0.394 | 5.57 |
| **BNNO-OH** | 5 | 1.194 | 1.472 | -0.278 | 8.12 |
| **BNNO-OH** | 6 | 1.245 | 1.407 | -0.163 | 7.65 |
| **BNNO-OH** | 7 | 1.295 | 1.343 | -0.047 | 8.66 |
| **BNNO-OH** | 8 | 1.346 | 1.278 | 0.068 | 8.84 |

| | | | | | |
|---|---|---|---|---|---|
| **BNNO-OH** | 9 | 1.397 | 1.214 | 0.184 | 8.33 |
| **BNNO-OH** | 10 | 1.448 | 1.149 | 0.299 | 7.55 |
| **BNNO-OH** | 11 | 1.499 | 1.085 | 0.415 | 7.22 |
| **BNNO-OH** | 12 | 1.550 | 1.020 | 0.530 | 8.48 |
| **BNNS-OH** | 1 | 1.010 | 1.650 | -0.640 | 0.01 |
| **BNNS-OH** | 2 | 1.073 | 1.569 | -0.496 | 1.16 |
| **BNNS-OH** | 3 | 1.136 | 1.487 | -0.351 | 3.25 |
| **BNNS-OH** | 4 | 1.199 | 1.406 | -0.207 | 5.16 |
| **BNNS-OH** | 5 | 1.261 | 1.324 | -0.063 | 6.20 |
| **BNNS-OH** | 6 | 1.324 | 1.243 | 0.081 | 6.19 |
| **BNNS-OH** | 7 | 1.387 | 1.161 | 0.226 | 5.55 |
| **BNNS-OH** | 8 | 1.450 | 1.080 | 0.370 | 5.48 |

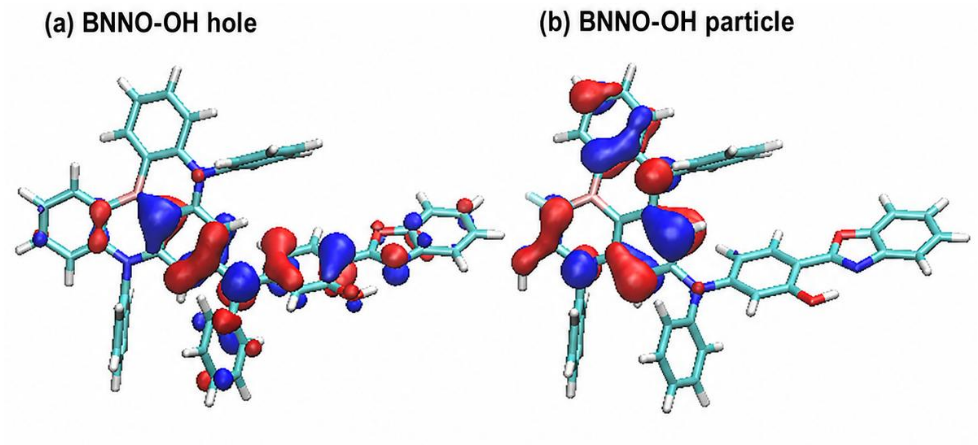
## S4.5 TD-DFT/NTO analyses

TD-DFT/NTO analyses were performed for the hydrogen-bonded conformers and optimized S1-enol*/S1-keto* geometries. The low-lying excited states are dominated by well-defined NTO pairs. The keto* structures are not dark states; therefore, the absence of classical dual emission is more consistently attributed to the shallow and higher-lying keto* basin rather than to a dark keto* state.

**Table S8**. TD-DFT/NTO summary for S1-S3 states.

| Geometry | State | Energy / eV | lambda / nm | fosc | Dominant NTO weight |
|---|---|---|---|---|---|
| **BNNO** S0-enol(HB) | S1 | 3.635 | 341.1 | 0.274 | 0.882 |
| **BNNO** S0-enol(HB) | S2 | 3.707 | 334.5 | 1.710 | 0.867 |
| **BNNO** S0-enol(HB) | S3 | 4.202 | 295.0 | 0.419 | 0.812 |
| **BNNO** S1-enol* | S1 | 3.528 | 351.4 | 0.417 | 0.928 |
| **BNNO** S1-enol* | S2 | 3.767 | 329.1 | 1.731 | 0.900 |
| **BNNO** S1-enol* | S3 | 4.201 | 295.1 | 0.332 | 0.784 |
| **BNNO** S1-keto* | S1 | 3.230 | 383.9 | 1.090 | 0.943 |
| **BNNO** S1-keto* | S2 | 3.613 | 343.2 | 0.439 | 0.911 |
| **BNNO** S1-keto* | S3 | 3.621 | 342.4 | 0.470 | 0.849 |
| **BNNS** S0-enol(HB) | S1 | 3.573 | 347.0 | 1.147 | 0.898 |
| **BNNS** S0-enol(HB) | S2 | 3.651 | 339.6 | 0.850 | 0.880 |
| **BNNS** S0-enol(HB) | S3 | 4.165 | 297.7 | 0.409 | 0.787 |
| **BNNS** S1-enol* | S1 | 3.212 | 386.0 | 1.414 | 0.943 |
| **BNNS** S1-enol* | S2 | 3.618 | 342.7 | 0.601 | 0.922 |
| **BNNS** S1-enol* | S3 | 4.026 | 307.9 | 0.249 | 0.578 |
| **BNNS** S1-keto* | S1 | 3.056 | 405.7 | 1.138 | 0.952 |

| | | | | | |
|---|---|---|---|---|---|
| **BNNS** S1-keto* | S2 | 3.514 | 352.8 | 0.299 | 0.954 |
| **BNNS** S1-keto* | S3 | 3.615 | 343.0 | 0.531 | 0.921 |


(a) BNNO-OH hole
(b) BNNO-OH particle

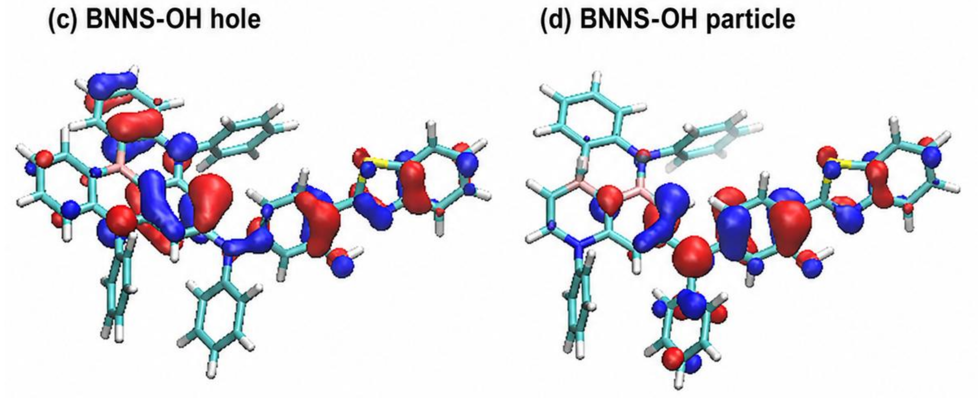

(c) BNNS-OH hole
(d) BNNS-OH particle

**Figure S3**. Representative S1 NTO hole and particle distributions. Representative NTO hole and particle distributions for the S1 states of the hydrogen-bonded S0-enol conformers of **BNNO-OH** and **BNNS-OH**, calculated at the TDA-CAM-B3LYP/def2-SVP/SMD(toluene) level. The dominant NTO pair contributions are 0.882 for **BNNO-OH** and 0.898 for **BNNS-OH**. Isosurface value: 0.03 a.u.

## S4.6 Cartesian coordinates of optimized structures

Cartesian coordinates are provided for the optimized structures used in the ESIPT analysis. All coordinates are given in Angstrom.

**BNNO-OH** S0 hydrogen-bonded enol
Method/geometry source: M06-2X/6-31G(d)/SMD(toluene)
Charge and multiplicity: 0 1

| | | | |
|---|---|---|---|
| C | -2.976720 | -0.389300 | -0.256290 |
| C | -1.924550 | -1.303510 | -0.138580 |
| C | -0.680530 | -0.853400 | 0.305380 |
| C | -0.450610 | 0.492680 | 0.591990 |
| C | -1.476400 | 1.419170 | 0.374170 |
| C | -2.767750 | 0.994520 | -0.028020 |
| N | -4.244550 | -0.835070 | -0.628440 |
| N | -1.238770 | 2.777270 | 0.583360 |
| N | 0.359890 | -1.796260 | 0.489480 |
| C | -4.399490 | -2.237360 | -0.901900 |
| C | -5.388520 | -0.024610 | -0.627550 |
| C | 0.073620 | 3.157100 | 1.029060 |
| C | -2.154380 | 3.788890 | 0.261480 |
| C | -5.297980 | 1.369870 | -0.387110 |
| C | -6.508350 | 2.084600 | -0.279860 |
| C | -7.745730 | 1.495850 | -0.466500 |
| C | -7.801870 | 0.133870 | -0.776030 |
| C | -6.647290 | -0.623090 | -0.849190 |
| C | -1.741330 | 5.135310 | 0.352540 |
| C | -2.593400 | 6.153620 | -0.032670 |
| C | -3.867470 | 5.869240 | -0.532550 |
| C | -4.279380 | 4.550350 | -0.591550 |
| C | -3.468430 | 3.476850 | -0.170430 |
| C | 1.102240 | 3.302910 | 0.100270 |
| C | 2.379290 | 3.642130 | 0.537590 |
| C | 2.622100 | 3.840970 | 1.895810 |
| C | 1.587960 | 3.698590 | 2.818260 |
| C | 0.309600 | 3.352020 | 2.386640 |
| C | -4.587590 | -3.129960 | 0.151500 |
| C | -4.713220 | -4.490040 | -0.115590 |
| C | -4.658480 | -4.951530 | -1.429830 |
| C | -4.474090 | -4.053130 | -2.478420 |
| C | -4.339780 | -2.691690 | -2.216020 |
| C | 1.702330 | -1.460730 | 0.243520 |
| B | -3.892020 | 1.989010 | -0.203070 |
| C | 2.718170 | -2.027080 | 1.013630 |
| C | 4.056540 | -1.715470 | 0.772940 |

|  |  |  |  |
|---|---|---|---|
| C | 4.388810 | -0.804760 | -0.255430 |
| C | 3.355360 | -0.244800 | -1.023460 |
| C | 2.035050 | -0.563990 | -0.794770 |
| C | 5.774580 | -0.473920 | -0.498520 |
| O | 6.075690 | 0.402040 | -1.493810 |
| C | 7.440350 | 0.502280 | -1.470570 |
| C | 7.907210 | -0.327220 | -0.449000 |
| N | 6.807360 | -0.933690 | 0.148990 |
| C | 8.260790 | 1.265810 | -2.281570 |
| C | 9.625580 | 1.163970 | -2.020590 |
| C | 10.120620 | 0.337460 | -0.999470 |
| C | 9.274930 | -0.421150 | -0.197090 |
| O | 4.975300 | -2.296640 | 1.557850 |
| H | 5.872130 | -1.986440 | 1.292090 |
| C | 0.033060 | -3.094710 | 0.978090 |
| C | -0.821870 | -3.236990 | 2.074470 |
| C | -1.160290 | -4.506260 | 2.531270 |
| C | -0.636640 | -5.640640 | 1.914310 |
| C | 0.224690 | -5.496540 | 0.828880 |
| C | 0.553000 | -4.231170 | 0.353520 |
| H | -8.760230 | -0.350190 | -0.941020 |
| H | -6.721660 | -1.682910 | -1.059030 |
| H | -8.656590 | 2.078130 | -0.371310 |
| H | -6.466330 | 3.134350 | -0.010040 |
| H | -5.256180 | 4.328270 | -1.007480 |
| H | -4.518740 | 6.668790 | -0.870650 |
| H | -2.250620 | 7.181980 | 0.037630 |
| H | -0.747950 | 5.381550 | 0.706620 |
| H | -0.508860 | 3.228720 | 3.089720 |
| H | 1.776360 | 3.851240 | 3.876320 |
| H | 3.619050 | 4.104250 | 2.235150 |
| H | 3.185220 | 3.749060 | -0.181860 |
| H | 0.891790 | 3.140540 | -0.953220 |
| H | 1.252650 | -0.135890 | -1.410080 |
| H | 2.491210 | -2.714620 | 1.820540 |
| H | 3.612410 | 0.440940 | -1.824640 |
| H | 9.654000 | -1.060890 | 0.592410 |
| H | 11.192110 | 0.290830 | -0.833760 |
| H | 10.322110 | 1.738130 | -2.622730 |
| H | 7.864120 | 1.898910 | -3.067060 |
| H | 1.213050 | -4.114980 | -0.500830 |
| H | 0.635270 | -6.373610 | 0.337990 |
| H | -0.896620 | -6.629820 | 2.277710 |
| H | -1.826630 | -4.606580 | 3.382770 |

| | | | |
|---|---|---|---|
| H | -1.220510 | -2.349690 | 2.557000 |
| H | -2.056800 | -2.353260 | -0.360720 |
| H | 0.518350 | 0.797730 | 0.962000 |
| H | -4.189220 | -1.974970 | -3.017910 |
| H | -4.429280 | -4.411430 | -3.502100 |
| H | -4.756940 | -6.012760 | -1.636150 |
| H | -4.851610 | -5.189580 | 0.702810 |
| H | -4.622690 | -2.749860 | 1.168580 |

**BNNO-OH** S1-enol*

Method/geometry source: TDA-CAM-B3LYP/def2-SVP/SMD(toluene)

Charge and multiplicity: 0 1

| | | | |
|---|---|---|---|
| C | -2.892973 | -0.353201 | -0.293462 |
| C | -1.829965 | -1.253613 | -0.075480 |
| C | -0.630776 | -0.809736 | 0.486503 |
| C | -0.492084 | 0.543104 | 0.820734 |
| C | -1.530475 | 1.455416 | 0.545807 |
| C | -2.758435 | 1.026952 | -0.009669 |
| N | -4.092990 | -0.824924 | -0.821150 |
| N | -1.352979 | 2.807237 | 0.846332 |
| N | 0.416994 | -1.728204 | 0.743582 |
| C | -4.171710 | -2.224056 | -1.147824 |
| C | -5.246504 | -0.044835 | -0.998075 |
| C | -0.133927 | 3.189454 | 1.508254 |
| C | -2.255048 | 3.820314 | 0.495694 |
| C | -5.223524 | 1.359392 | -0.716876 |
| C | -6.456323 | 2.033778 | -0.832890 |
| C | -7.626836 | 1.409537 | -1.256005 |
| C | -7.606930 | 0.055653 | -1.579200 |
| C | -6.425985 | -0.669328 | -1.443505 |
| C | -1.900409 | 5.160833 | 0.740012 |
| C | -2.741016 | 6.200090 | 0.352218 |
| C | -3.939744 | 5.914378 | -0.297171 |
| C | -4.303747 | 4.589383 | -0.519931 |
| C | -3.512732 | 3.495398 | -0.111436 |
| C | 1.000448 | 3.500196 | 0.760373 |
| C | 2.177431 | 3.858568 | 1.411529 |
| C | 2.219955 | 3.908851 | 2.803597 |
| C | 1.082524 | 3.599489 | 3.546149 |
| C | -0.097113 | 3.238908 | 2.900007 |
| C | -4.561870 | -3.144062 | -0.176460 |
| C | -4.623641 | -4.497661 | -0.495192 |
| C | -4.299286 | -4.929522 | -1.779848 |
| C | -3.911480 | -4.005273 | -2.747481 |
| C | -3.846710 | -2.650112 | -2.433743 |

|  |  |  |  |
|---|---|---|---|
| C | 1.723312 | -1.462021 | 0.328854 |
| B | -3.879462 | 2.000914 | -0.288208 |
| C | 2.815107 | -2.043037 | 0.983444 |
| C | 4.124508 | -1.785958 | 0.576273 |
| C | 4.360477 | -0.903362 | -0.509672 |
| C | 3.256649 | -0.325160 | -1.158024 |
| C | 1.963838 | -0.593750 | -0.763596 |
| C | 5.719382 | -0.633044 | -0.907527 |
| O | 5.969626 | 0.218782 | -1.929487 |
| C | 7.329945 | 0.257587 | -2.039440 |
| C | 7.854923 | -0.590956 | -1.060360 |
| N | 6.790282 | -1.138223 | -0.361877 |
| C | 8.106709 | 0.981116 | -2.927342 |
| C | 9.485321 | 0.820156 | -2.797534 |
| C | 10.036793 | -0.026535 | -1.822834 |
| C | 9.236060 | -0.744898 | -0.940109 |
| O | 5.118739 | -2.373934 | 1.236116 |
| H | 5.981026 | -2.087287 | 0.838553 |
| C | 0.094817 | -2.920243 | 1.455561 |
| C | -0.602674 | -2.844029 | 2.664733 |
| C | -0.946150 | -4.005793 | 3.349376 |
| C | -0.588549 | -5.253281 | 2.842540 |
| C | 0.108402 | -5.330816 | 1.638170 |
| C | 0.441967 | -4.173665 | 0.941475 |
| H | -8.510979 | -0.449019 | -1.926204 |
| H | -6.431760 | -1.731074 | -1.678476 |
| H | -8.553274 | 1.983037 | -1.335144 |
| H | -6.505827 | 3.087956 | -0.565805 |
| H | -5.236661 | 4.395023 | -1.046115 |
| H | -4.595053 | 6.723587 | -0.627532 |
| H | -2.445638 | 7.232808 | 0.548996 |
| H | -0.957074 | 5.400699 | 1.224937 |
| H | -0.996147 | 2.993810 | 3.468646 |
| H | 1.112192 | 3.637024 | 4.637114 |
| H | 3.144846 | 4.189485 | 3.311929 |
| H | 3.067681 | 4.098852 | 0.826550 |
| H | 0.954174 | 3.457702 | -0.329406 |
| H | 1.128976 | -0.149340 | -1.302955 |
| H | 2.675360 | -2.708992 | 1.833427 |
| H | 3.434355 | 0.340418 | -2.004467 |
| H | 9.663617 | -1.402535 | -0.181906 |
| H | 11.122657 | -0.121925 | -1.757682 |
| H | 10.151017 | 1.365095 | -3.469827 |
| H | 7.664478 | 1.635227 | -3.679692 |

| | | | |
|---|---|---|---|
| H | 0.977666 | -4.236243 | -0.007240 |
| H | 0.387028 | -6.304220 | 1.228233 |
| H | -0.853551 | -6.163674 | 3.384211 |
| H | -1.489824 | -3.933110 | 4.293994 |
| H | -0.873509 | -1.866094 | 3.066499 |
| H | -1.924903 | -2.304553 | -0.334280 |
| H | 0.431650 | 0.872079 | 1.289092 |
| H | -3.543820 | -1.915092 | -3.181813 |
| H | -3.655833 | -4.340196 | -3.754978 |
| H | -4.348098 | -5.992015 | -2.027521 |
| H | -4.925732 | -5.219399 | 0.266559 |
| H | -4.812190 | -2.792674 | 0.826249 |

**BNNO-OH** S1-keto*

Method/geometry source: TDA-CAM-B3LYP/def2-SVP/SMD(toluene)

Charge and multiplicity: 0 1

| | | | |
|---|---|---|---|
| C | -2.999706 | -0.418911 | -0.207955 |
| C | -1.987240 | -1.363806 | -0.020521 |
| C | -0.721641 | -0.948174 | 0.410050 |
| C | -0.454184 | 0.408687 | 0.640341 |
| C | -1.451198 | 1.362800 | 0.410761 |
| C | -2.748376 | 0.968473 | -0.010801 |
| N | -4.265321 | -0.832127 | -0.618640 |
| N | -1.173868 | 2.713756 | 0.617679 |
| N | 0.306002 | -1.884121 | 0.592768 |
| C | -4.457481 | -2.229665 | -0.890603 |
| C | -5.374955 | 0.020945 | -0.709564 |
| C | 0.119547 | 3.059742 | 1.139291 |
| C | -2.053899 | 3.747282 | 0.276125 |
| C | -5.250185 | 1.417663 | -0.493371 |
| C | -6.440044 | 2.175673 | -0.492484 |
| C | -7.683771 | 1.627175 | -0.750531 |
| C | -7.770440 | 0.261855 | -1.030459 |
| C | -6.639012 | -0.533128 | -1.005721 |
| C | -1.615964 | 5.084829 | 0.395559 |
| C | -2.426039 | 6.130833 | -0.004995 |
| C | -3.690116 | 5.882626 | -0.545896 |
| C | -4.132679 | 4.574850 | -0.630658 |
| C | -3.362821 | 3.472898 | -0.201058 |
| C | 1.191106 | 3.268882 | 0.272187 |
| C | 2.443498 | 3.594727 | 0.785229 |
| C | 2.626207 | 3.712313 | 2.161806 |
| C | 1.553631 | 3.503060 | 3.025771 |
| C | 0.299698 | 3.175716 | 2.515974 |
| C | -4.822070 | -3.098825 | 0.136726 |

| | | | |
|---|---|---|---|
| C | -5.001711 | -4.452833 | -0.132081 |
| C | -4.819012 | -4.939155 | -1.425273 |
| C | -4.454910 | -4.068464 | -2.450026 |
| C | -4.272811 | -2.713631 | -2.184110 |
| C | 1.637963 | -1.512804 | 0.309105 |
| B | -3.832402 | 1.995426 | -0.243962 |
| C | 2.688478 | -1.831752 | 1.182179 |
| C | 4.031371 | -1.489458 | 0.895467 |
| C | 4.275814 | -0.749693 | -0.377255 |
| C | 3.205254 | -0.445255 | -1.233100 |
| C | 1.906390 | -0.834215 | -0.904111 |
| C | 5.607044 | -0.387468 | -0.664813 |
| O | 5.993672 | 0.305175 | -1.764034 |
| C | 7.343398 | 0.480061 | -1.676976 |
| C | 7.802710 | -0.123232 | -0.489750 |
| N | 6.691304 | -0.650603 | 0.099757 |
| C | 8.178942 | 1.126641 | -2.565164 |
| C | 9.537538 | 1.156944 | -2.224181 |
| C | 10.008986 | 0.562479 | -1.047032 |
| C | 9.158356 | -0.089522 | -0.154267 |
| O | 4.997591 | -1.755199 | 1.659029 |
| H | 6.471403 | -1.170476 | 0.982557 |
| C | 0.027644 | -3.187068 | 1.080384 |
| C | -0.855048 | -3.374681 | 2.151028 |
| C | -1.115922 | -4.655517 | 2.625898 |
| C | -0.492064 | -5.762323 | 2.053442 |
| C | 0.395182 | -5.576038 | 0.994638 |
| C | 0.653459 | -4.300302 | 0.506556 |
| H | -8.737229 | -0.195223 | -1.254855 |
| H | -6.739947 | -1.597870 | -1.203557 |
| H | -8.580014 | 2.250478 | -0.735845 |
| H | -6.384548 | 3.237719 | -0.257616 |
| H | -5.111971 | 4.389996 | -1.070021 |
| H | -4.317409 | 6.705443 | -0.894322 |
| H | -2.058471 | 7.155426 | 0.090283 |
| H | -0.626798 | 5.305413 | 0.790477 |
| H | -0.548697 | 3.006591 | 3.181890 |
| H | 1.693127 | 3.592517 | 4.105185 |
| H | 3.609645 | 3.966310 | 2.563140 |
| H | 3.282403 | 3.755690 | 0.104815 |
| H | 1.036070 | 3.172171 | -0.804042 |
| H | 1.090523 | -0.637546 | -1.600083 |
| H | 2.500658 | -2.358011 | 2.118108 |
| H | 3.393153 | 0.083064 | -2.169006 |

| | | | |
|---|---|---|---|
| H | 9.527503 | -0.551738 | 0.761554 |
| H | 11.076268 | 0.610266 | -0.820737 |
| H | 10.242781 | 1.655253 | -2.891928 |
| H | 7.795934 | 1.585154 | -3.477268 |
| H | 1.342864 | -4.157765 | -0.326647 |
| H | 0.888462 | -6.435840 | 0.535688 |
| H | -0.693331 | -6.766125 | 2.433209 |
| H | -1.805348 | -4.786808 | 3.462972 |
| H | -1.332536 | -2.509692 | 2.613358 |
| H | -2.160884 | -2.418334 | -0.207842 |
| H | 0.525174 | 0.694370 | 1.009575 |
| H | -3.986393 | -2.020984 | -2.977860 |
| H | -4.310073 | -4.445460 | -3.464710 |
| H | -4.960081 | -6.001678 | -1.634773 |
| H | -5.285814 | -5.132203 | 0.674339 |
| H | -4.963306 | -2.706043 | 1.145471 |

**BNNS-OH** S0 hydrogen-bonded enol

Method/geometry source: TDA-CAM-B3LYP/def2-SVP/SMD(toluene) single-point geometry used for TD/NTO

Charge and multiplicity: 0 1

| | | | |
|---|---|---|---|
| C | 3.163510 | -0.405810 | -0.219090 |
| C | 2.116380 | -1.323330 | -0.083950 |
| C | 0.854270 | -0.864590 | 0.297420 |
| C | 0.614290 | 0.489600 | 0.535470 |
| C | 1.652650 | 1.409070 | 0.355090 |
| C | 2.951910 | 0.981000 | -0.014720 |
| N | 4.436960 | -0.856610 | -0.565620 |
| N | 1.410710 | 2.768790 | 0.548650 |
| N | -0.193590 | -1.800640 | 0.463880 |
| C | 4.633000 | -2.278310 | -0.639460 |
| C | 5.500870 | -0.009460 | -0.904130 |
| C | 0.050090 | 3.164320 | 0.789260 |
| C | 2.416420 | 3.743930 | 0.581420 |
| C | 5.378200 | 1.399490 | -0.795810 |
| C | 6.446870 | 2.177320 | -1.286660 |
| C | 7.612100 | 1.622540 | -1.783350 |
| C | 7.742420 | 0.230700 | -1.792990 |
| C | 6.705610 | -0.579360 | -1.368880 |
| C | 2.070870 | 5.068840 | 0.923330 |
| C | 3.051810 | 6.034830 | 1.048980 |
| C | 4.398800 | 5.715010 | 0.854800 |
| C | 4.728480 | 4.425820 | 0.478390 |
| C | 3.764580 | 3.414550 | 0.288460 |
| C | -0.795180 | 3.391390 | -0.293660 |

| | | | |
|---|---|---|---|
| C | -2.127460 | 3.727920 | -0.066790 |
| C | -2.607100 | 3.840100 | 1.236420 |
| C | -1.754090 | 3.617460 | 2.316020 |
| C | -0.422710 | 3.275380 | 2.094940 |
| C | 4.938440 | -2.985450 | 0.520150 |
| C | 5.093430 | -4.368050 | 0.461070 |
| C | 4.947490 | -5.035600 | -0.753030 |
| C | 4.644420 | -4.321370 | -1.910920 |
| C | 4.482380 | -2.939690 | -1.856380 |
| C | -1.531200 | -1.453430 | 0.201870 |
| B | 4.078880 | 1.973730 | -0.181660 |
| C | -2.560010 | -1.992060 | 0.971620 |
| C | -3.893800 | -1.661420 | 0.722710 |
| C | -4.215790 | -0.753950 | -0.316310 |
| C | -3.161210 | -0.232300 | -1.084850 |
| C | -1.847050 | -0.570360 | -0.852530 |
| C | -5.599310 | -0.382420 | -0.561900 |
| S | -6.048220 | 0.777960 | -1.820230 |
| C | -7.721940 | 0.575560 | -1.369390 |
| C | -7.814990 | -0.344180 | -0.308480 |
| N | -6.604030 | -0.858150 | 0.116480 |
| C | -8.855600 | 1.181350 | -1.908670 |
| C | -10.090420 | 0.850560 | -1.366760 |
| C | -10.194180 | -0.065450 | -0.308920 |
| C | -9.066770 | -0.667130 | 0.226540 |
| O | -4.817660 | -2.220570 | 1.514770 |
| H | -5.707690 | -1.894560 | 1.236040 |
| C | 0.109450 | -3.100310 | 0.964790 |
| C | 0.938810 | -3.249570 | 2.079570 |
| C | 1.249550 | -4.521580 | 2.548340 |
| C | 0.722480 | -5.651040 | 1.925580 |
| C | -0.114060 | -5.499770 | 0.821860 |
| C | -0.413810 | -4.232040 | 0.334390 |
| H | 5.326470 | -4.923290 | 1.364280 |
| H | 5.067720 | -6.113570 | -0.797030 |
| H | 4.527840 | -4.840530 | -2.857080 |
| H | 4.237760 | -2.365260 | -2.745290 |
| H | 5.042790 | -2.445930 | 1.456940 |
| H | 6.822920 | -1.655030 | -1.411730 |
| H | 8.656800 | -0.230480 | -2.155180 |
| H | 8.411720 | 2.254430 | -2.156330 |
| H | 6.337520 | 3.256320 | -1.299090 |
| H | 5.775220 | 4.172810 | 0.349590 |
| H | 5.170040 | 6.465530 | 0.995110 |

| | | | |
|---|---|---|---|
| H | 2.763810 | 7.045940 | 1.322300 |
| H | 1.037390 | 5.335970 | 1.106060 |
| H | 0.255540 | 3.086820 | 2.922220 |
| H | -2.127070 | 3.702150 | 3.331870 |
| H | -3.646950 | 4.097980 | 1.411210 |
| H | -2.791600 | 3.899950 | -0.908310 |
| H | -0.402000 | 3.293020 | -1.301400 |
| H | -0.365770 | 0.805130 | 0.864640 |
| H | 2.260580 | -2.378010 | -0.273340 |
| H | 1.340470 | -2.366140 | 2.566510 |
| H | 1.897420 | -4.627620 | 3.413220 |
| H | 0.960770 | -6.642140 | 2.298480 |
| H | -0.527330 | -6.373130 | 0.326640 |
| H | -1.054550 | -4.109890 | -0.533730 |
| H | -2.349940 | -2.672330 | 1.789340 |
| H | -1.057910 | -0.161980 | -1.472500 |
| H | -3.383850 | 0.449850 | -1.901930 |
| H | -8.776310 | 1.890210 | -2.726400 |
| H | -10.987830 | 1.309050 | -1.769490 |
| H | -11.172410 | -0.305390 | 0.095090 |
| H | -9.131050 | -1.377420 | 1.044350 |

**BNNS-OH** S1-enol*

Method/geometry source: TDA-CAM-B3LYP/def2-SVP/SMD(toluene)

Charge and multiplicity: 0 1

| | | | |
|---|---|---|---|
| C | 3.149122 | -0.445891 | -0.201668 |
| C | 2.147476 | -1.397420 | 0.004085 |
| C | 0.873413 | -0.976865 | 0.408269 |
| C | 0.588417 | 0.380119 | 0.616513 |
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| C | 2.890390 | 0.940590 | 0.002274 |
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| N | 1.309597 | 2.681187 | 0.635678 |
| N | -0.156460 | -1.915904 | 0.583502 |
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| C | -0.046171 | 3.034912 | 0.957825 |
| C | 2.281344 | 3.688639 | 0.615192 |
| C | 5.272793 | 1.439359 | -0.875549 |
| C | 6.302943 | 2.251786 | -1.394803 |
| C | 7.461528 | 1.736974 | -1.948630 |
| C | 7.626377 | 0.351197 | -1.993546 |
| C | 6.629019 | -0.490071 | -1.534109 |
| C | 1.909044 | 5.003534 | 0.970167 |
| C | 2.854655 | 6.009539 | 1.037909 |

|  |  |  |  |
|---|---|---|---|
| C | 4.198862 | 5.739740 | 0.767465 |
| C | 4.557333 | 4.460345 | 0.384150 |
| C | 3.626426 | 3.406588 | 0.258182 |
| C | -0.948907 | 3.310783 | -0.067125 |
| C | -2.269979 | 3.627628 | 0.239565 |
| C | -2.686943 | 3.672669 | 1.567940 |
| C | -1.780907 | 3.400084 | 2.591252 |
| C | -0.460654 | 3.078823 | 2.288330 |
| C | 5.156225 | -2.962309 | 0.374418 |
| C | 5.390320 | -4.331643 | 0.275657 |
| C | 5.132014 | -5.000371 | -0.918826 |
| C | 4.637854 | -4.297788 | -2.016399 |
| C | 4.401807 | -2.929139 | -1.920835 |
| C | -1.464743 | -1.579188 | 0.236876 |
| B | 3.976200 | 1.972808 | -0.213919 |
| C | -2.556463 | -1.964771 | 1.055282 |
| C | -3.845216 | -1.582792 | 0.745962 |
| C | -4.104959 | -0.777316 | -0.440708 |
| C | -2.989156 | -0.439300 | -1.265458 |
| C | -1.712478 | -0.824711 | -0.943777 |
| C | -5.423556 | -0.357847 | -0.726576 |
| S | -5.834708 | 0.664334 | -2.121767 |
| C | -7.505438 | 0.641782 | -1.619164 |
| C | -7.636242 | -0.140138 | -0.432854 |
| N | -6.487548 | -0.673998 | 0.028625 |
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| C | -10.003376 | 0.326737 | -0.459748 |
| C | -8.919437 | -0.287125 | 0.141705 |
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| C | 0.994944 | -3.320905 | 2.221535 |
| C | 1.244074 | -4.574737 | 2.763341 |
| C | 0.625633 | -5.708424 | 2.235459 |
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| C | -0.503006 | -4.330462 | 0.604007 |
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| H | 5.316413 | -6.074091 | -0.995311 |
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| H | 4.015110 | -2.367539 | -2.773482 |
| H | 5.356383 | -2.425626 | 1.303807 |
| H | 6.774849 | -1.565685 | -1.603558 |
| H | 8.539218 | -0.082648 | -2.408710 |

| | | | |
|---|---|---|---|
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| H | 6.175027 | 3.333304 | -1.380210 |
| H | 5.609463 | 4.255135 | 0.191626 |
| H | 4.952244 | 6.524937 | 0.855501 |
| H | 2.541067 | 7.016578 | 1.323163 |
| H | 0.873543 | 5.235114 | 1.209475 |
| H | 0.256750 | 2.857766 | 3.081098 |
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| H | -0.609760 | 3.270075 | -1.104001 |
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| H | 2.325549 | -2.452796 | -0.174908 |
| H | 1.463473 | -2.432654 | 2.646550 |
| H | 1.919972 | -4.666301 | 3.616111 |
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| H | -0.731210 | -6.462217 | 0.733851 |
| H | -1.177008 | -4.228753 | -0.247237 |
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| H | -0.882427 | -0.577187 | -1.605419 |
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| H | -8.485119 | 1.848148 | -3.124481 |
| H | -10.729056 | 1.565578 | -2.082930 |
| H | -10.996026 | 0.214747 | -0.017230 |
| H | -9.031402 | -0.881906 | 1.049908 |

**BNNS-OH** S1-keto*

Method/geometry source: TDA-CAM-B3LYP/def2-SVP/SMD(toluene)

Charge and multiplicity: 0 1

| | | | |
|---|---|---|---|
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| C | 2.167383 | -1.389272 | -0.001670 |
| C | 0.885184 | -0.973961 | 0.375708 |
| C | 0.603648 | 0.383859 | 0.575410 |
| C | 1.609605 | 1.338109 | 0.389788 |
| C | 2.917823 | 0.946456 | 0.002901 |
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| N | 1.324222 | 2.687802 | 0.592335 |
| N | -0.142279 | -1.915113 | 0.539816 |
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| C | -0.036873 | 3.045619 | 0.882810 |
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| C | 7.536035 | 1.723271 | -1.841346 |

| | | | |
|---|---|---|---|
| C | 7.697960 | 0.336580 | -1.876268 |
| C | 6.687472 | -0.499604 | -1.438219 |
| C | 1.915534 | 5.012492 | 0.929244 |
| C | 2.858258 | 6.020139 | 1.009901 |
| C | 4.207353 | 5.751058 | 0.765309 |
| C | 4.573820 | 4.469771 | 0.395309 |
| C | 3.647282 | 3.414189 | 0.257585 |
| C | -0.912005 | 3.334655 | -0.162277 |
| C | -2.236986 | 3.663082 | 0.113578 |
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| C | -3.871047 | -1.525990 | 0.807340 |
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| C | -3.030181 | -0.465848 | -1.291677 |
| C | -1.733810 | -0.861558 | -0.967076 |
| C | -5.442368 | -0.345777 | -0.741832 |
| S | -5.945936 | 0.642114 | -2.097073 |
| C | -7.603194 | 0.608808 | -1.525879 |
| C | -7.701208 | -0.155064 | -0.335945 |
| N | -6.502094 | -0.659291 | 0.046291 |
| C | -8.723812 | 1.209247 | -2.088317 |
| C | -9.953477 | 1.043975 | -1.453054 |
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| C | -8.945659 | -0.314395 | 0.297074 |
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| H | -6.209024 | -1.219828 | 0.894712 |
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| C | 0.973211 | -3.376304 | 2.159443 |
| C | 1.229945 | -4.649429 | 2.657281 |
| C | 0.641737 | -5.768878 | 2.072120 |
| C | -0.204617 | -5.603832 | 0.976955 |
| C | -0.456965 | -4.335953 | 0.465644 |
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| H | 5.340260 | -6.077946 | -0.919490 |
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| H | 5.337095 | -2.424788 | 1.372480 |
| H | 6.832010 | -1.575911 | -1.499064 |
| H | 8.619676 | -0.101652 | -2.266615 |
| H | 8.318402 | 2.384795 | -2.218436 |
| H | 6.240700 | 3.325063 | -1.311918 |
| H | 5.629673 | 4.265086 | 0.223900 |
| H | 4.958323 | 6.537434 | 0.863294 |
| H | 2.538023 | 7.027960 | 1.285050 |
| H | 0.875763 | 5.244335 | 1.148939 |
| H | 0.211591 | 2.854309 | 3.011453 |
| H | -2.157852 | 3.447206 | 3.509318 |
| H | -3.726158 | 3.960289 | 1.646752 |
| H | -2.923191 | 3.883614 | -0.706903 |
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| H | -3.198570 | 0.069143 | -2.229345 |
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| H | -10.845672 | 1.506923 | -1.878663 |
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| H | -9.022057 | -0.900674 | 1.213967 |

## S5. Photophysical Properties

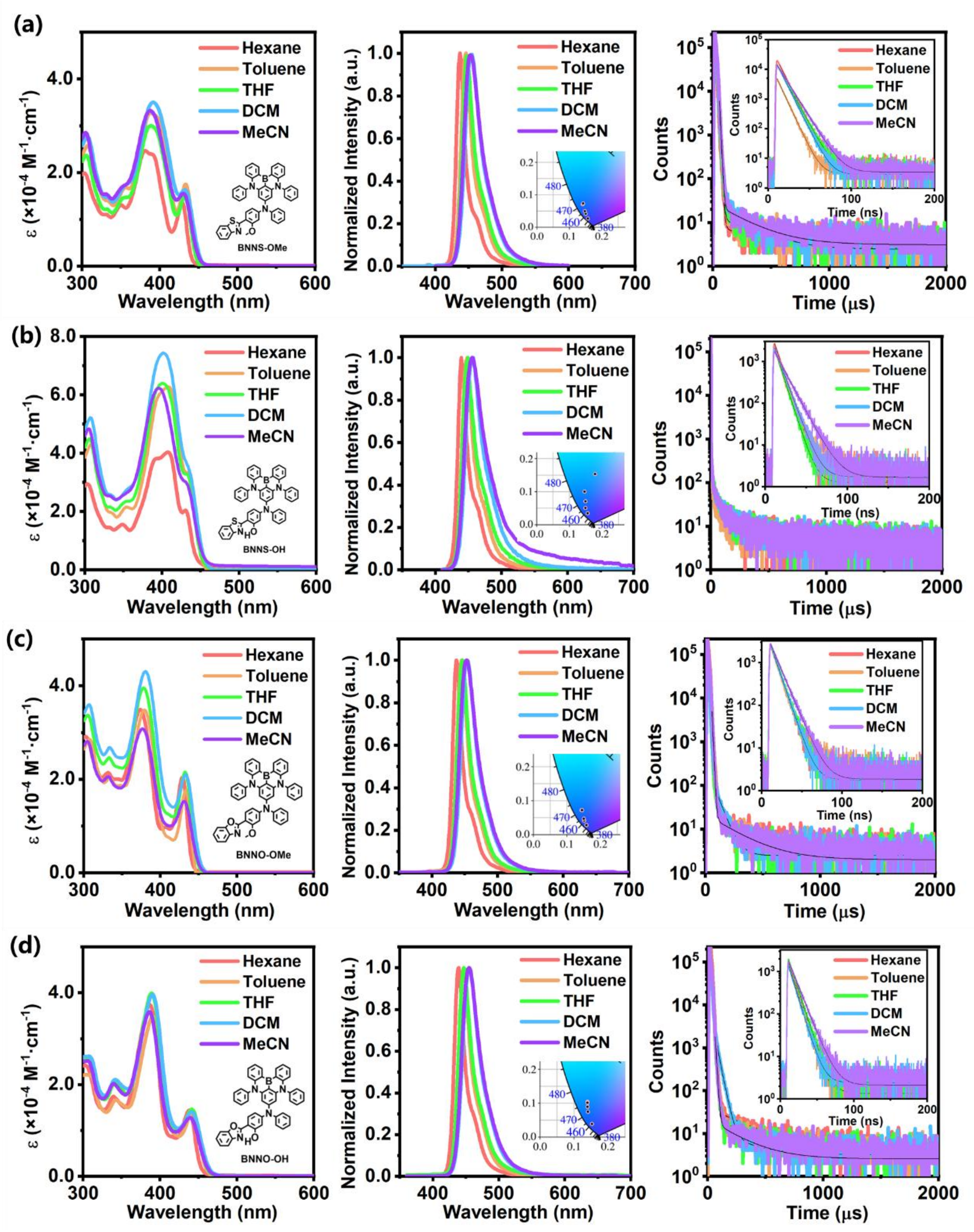


**Figure S4.** UV-Vis, photoluminescent spectra and transient PL decay curves in oxygen-free solvents ($1\times10^{-5}$ M) at 298 K of (a) **BNNS-OMe**, (b) **BNNS-OH**, (c) **BNNO-OMe**, (d) **BNNO-OH**, inset: the corresponding structures and CIE coordinates.

**Table S9** Photophysical parameters of the compounds in different solvents under oxygen-free condition.

| Compounds | Solvents | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | FWHM [nm] | $\tau_{PF}$[ns]/ $\tau_{DF}$[μs] | PLQY |
|---|---|---|---|---|---|---|
| **BNNS-OMe** | Hexane | 380,428 | 437 | 15 | 7.8/207.9 | 0.70 |
| | Toluene | 388,433 | 446 | 19 | 7.2/221.0 | 0.72 |
| | THF | 389,432 | 448 | 21 | 8.1/293.3 | 0.73 |
| | DCM | 390,432 | 455 | 29 | 7.7/208.3 | 0.67 |
| | MeCN | 388,429 | 454 | 31 | 9.6/252.9 | 0.71 |
| **BNNS-OH** | Hexane | 408,428 | 439 | 17 | 7.5/198.6 | 0.61 |
| | Toluene | 408,433 | 448 | 21 | 8.2/203.1 | 0.65 |
| | THF | 399,432 | 448 | 26 | 7.3/196.9 | 0.56 |
| | DCM | 401,432 | 456 | 32 | 8.1/179.4 | 0.52 |
| | MeCN | 396,429 | 457 | 38 | 11.4/180.0 | 0.31 |
| **BNNO-OMe** | Hexane | 374,429 | 437 | 17 | 7.7/243.0 | 0.71 |
| | Toluene | 379,433 | 445 | 21 | 7.9/198.1 | 0.74 |
| | THF | 378,432 | 446 | 22 | 8.2/97.0 | 0.75 |
| | DCM | 380,433 | 454 | 29 | 7.8/60.4 | 0.68 |
| | MeCN | 376,431 | 453 | 32 | 9.6/242.8 | 0.73 |
| **BNNO-OH** | Hexane | 386,438 | 439 | 18 | 7.9/326.0 | 0.60 |
| | Toluene | 391,442 | 447 | 21 | 7.2/306.3 | 0.63 |
| | THF | 389,441 | 447 | 24 | 8.1/240.6 | 0.65 |
| | DCM | 390,441 | 455 | 31 | 7.7/223.1 | 0.60 |
| | MeCN | 386,439 | 455 | 33 | 9.6/230.0 | 0.61 |

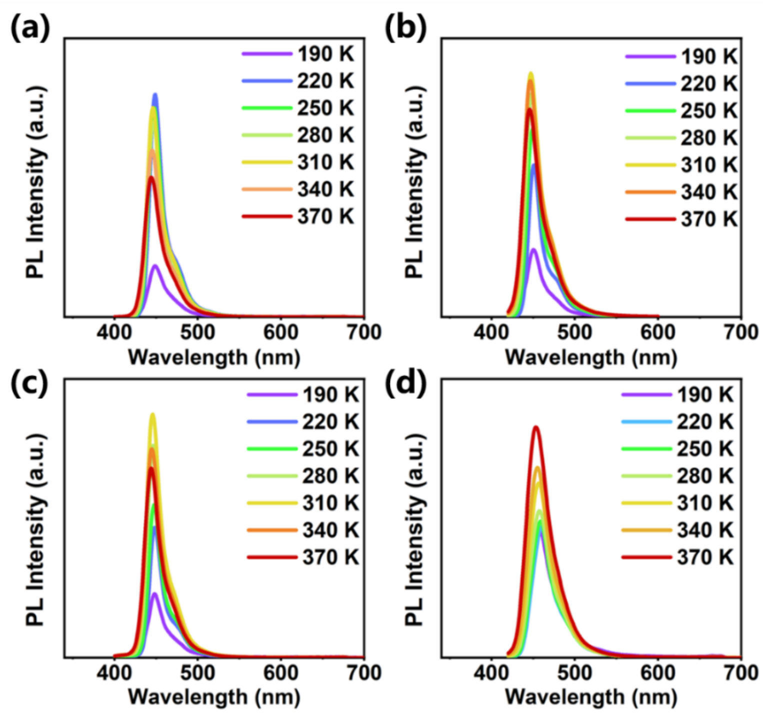


**Figure S5.** Temperature dependent PL spectra of (a) **BNNS-OMe**, (b) **BNNS-OH**, (c) **BNNO-OMe**, (d) **BNNO-OH** in oxygen-free toluene (1×10$^{-5}$ M).

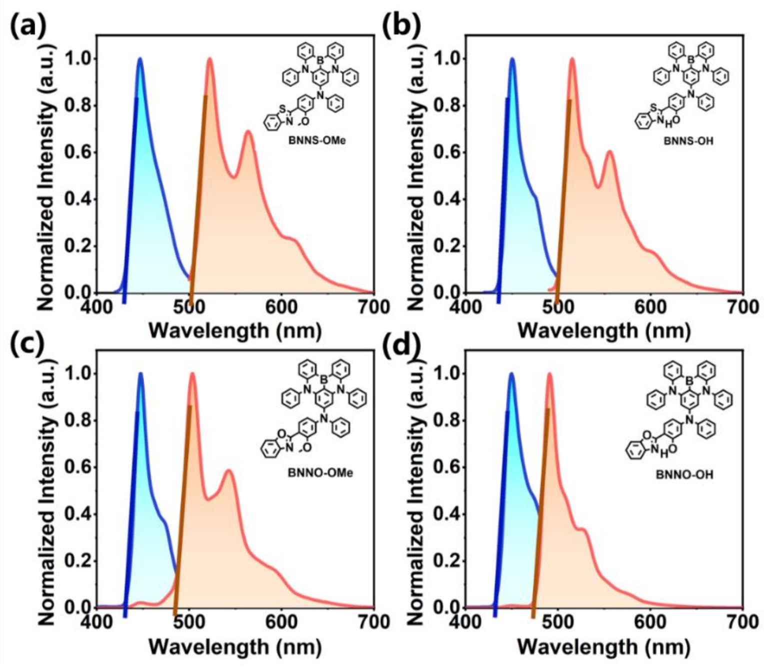


**Figure S6.** Normalized fluorescence and phosphorescence spectra at 77 K of (a) **BNNS-OMe**, (b) **BNNS-OH**, (c) **BNNO-OMe**, (d) **BNNO-OH** in oxygen-free toluene (1×10$^{-5}$ M, delay time of phosphorescence spectra: 1 ms).

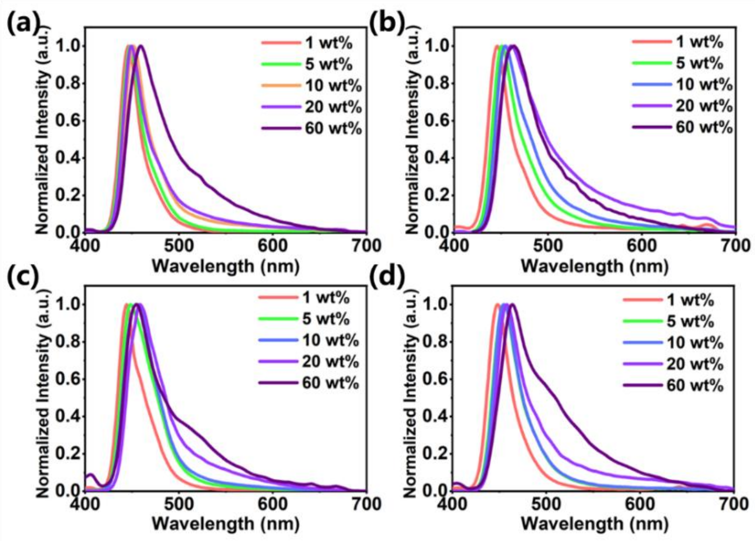


**Figure S7.** Fluorescence spectra of (a) **BNNS-OMe**, (b) **BNNS-OH**, (c) **BNNO-OMe**, (d) **BNNO-OH** doped into PMMA matrix at various doping ratios ($\lambda_{ex}$ = 365 nm).

**Table S10.** Photophysical parameters of the compounds doped into PMMA matrix at various doping ratios.

| Compounds | Doping Ratio | $\lambda_{em}$ [nm] | PLQY |
|---|---|---|---|
| **BNNS-OMe** | 1 wt% | 447 | 0.41 |
| | 5 wt% | 449 | 0.29 |
| | 10 wt% | 452 | 0.16 |
| | 20 wt% | 449 | 0.05 |
| | 60 wt% | 459 | 0.02 |
| **BNNS-OH** | 1 wt% | 446 | 0.21 |
| | 5 wt% | 449 | 0.17 |
| | 10 wt% | 454 | 0.09 |
| | 20 wt% | 461 | 0.05 |
| | 60 wt% | 463 | 0.01 |
| **BNNO-OMe** | 1 wt% | 445 | 0.46 |
| | 5 wt% | 449 | 0.37 |
| | 10 wt% | 450 | 0.25 |
| | 20 wt% | 450 | 0.12 |
| | 60 wt% | 454 | 0.02 |
| **BNNO-OH** | 1 wt% | 448 | 0.25 |
| | 5 wt% | 455 | 0.22 |
| | 10 wt% | 455 | 0.15 |
| | 20 wt% | 458 | 0.06 |
| | 60 wt% | 464 | 0.02 |

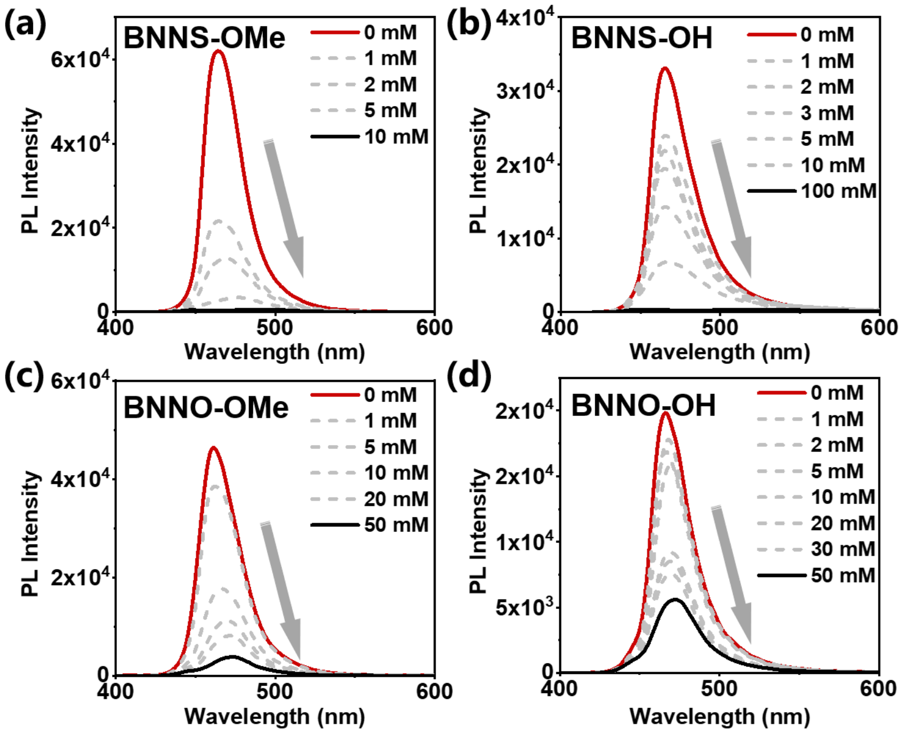


**Figure S8.** Emission spectral changes of (a) **BNNS-OMe**, (b) **BNNS-OH**, (c) **BNNO-OMe**, (d) **BNNO-OH** upon addition of DECP in toluene ($1\times10^{-3}$ M, $\lambda_{ex}$ = 365 nm).

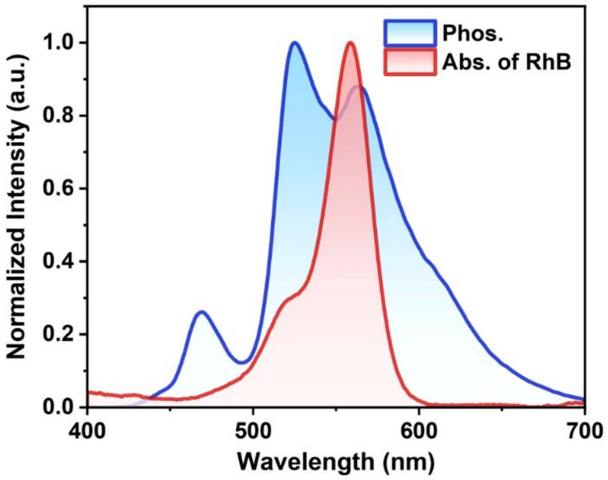


**Figure S9.** Phosphorescence emission spectra of **BNNS-OMe**/TPA at a doping ratio of 1000:1 (delay time: 1 ms) and the absorption spectrum of RhB in $1\times10^{-5}$ M DCM solution.

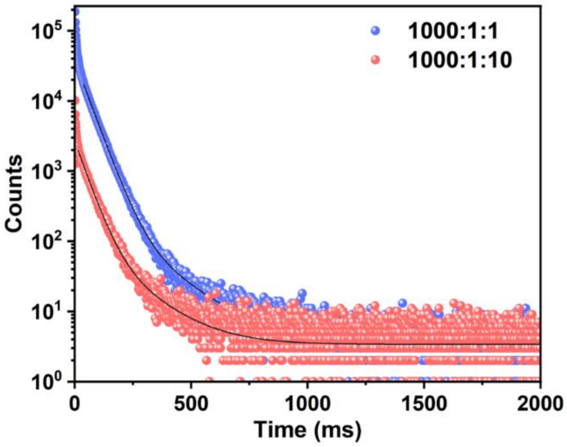
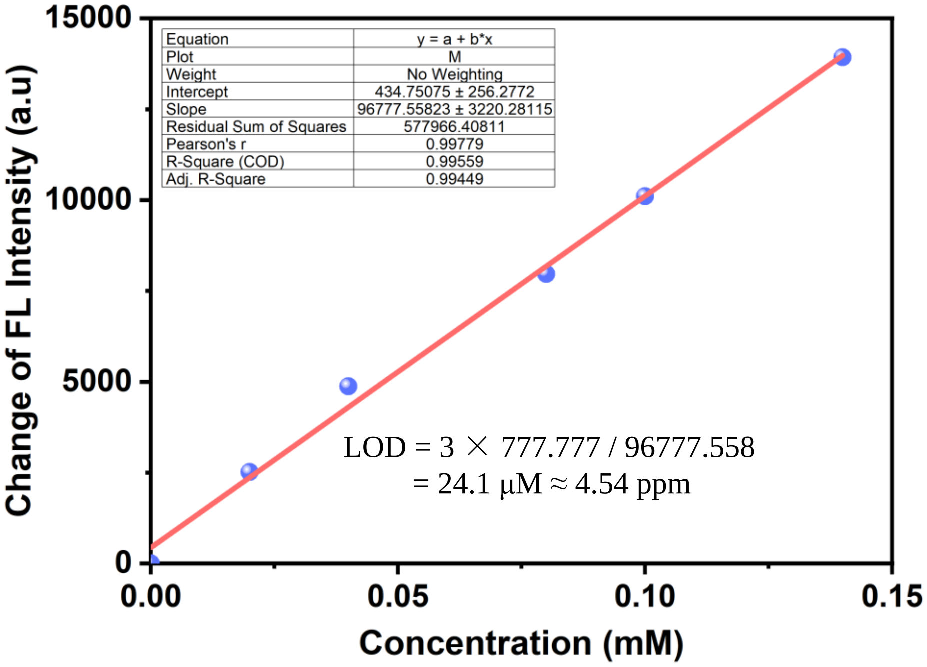


**Figure S10.** Phosphorescence decay spectra of TPA/**BNNS-OMe**/RhB with different doping ratios at 592 nm and 624 nm (delay time: 1 ms).



| | |
|---|---|
| Equation | y = a + b*x |
| Plot | M |
| Weight | No Weighting |
| Intercept | 434.75075 ± 256.2772 |
| Slope | 96777.55823 ± 3220.28115 |
| Residual Sum of Squares | 577966.40811 |
| Pearson's r | 0.99779 |
| R-Square (COD) | 0.99559 |
| Adj. R-Square | 0.99449 |

$$\text{LOD} = 3 \times 777.777 / 96777.558$$
$$= 24.1\ \mu\text{M} \approx 4.54\ \text{ppm}$$

**Figure S11.** Limit of detection (LOD) of BNNS-OMe for DECP in toluene.

## S6. Thermal and Electrochemical Characterization

Thermal gravimetric analysis (TGA) was tested on TA TGA thermal analysis system from 30 °C to 800 °C. The heating rate was 20 °C/min. Cyclic voltammetry (CV) was recorded at room temperature on an AUTOLAB-CV-75W voltammetric analyzer with ferrocene as the internal standard and tetrabutyl ammonium hexafluorophosphate (0.1 M) in deaerated DCM or THF as the supporting electrolyte solvent. The cyclic voltammograms were obtained at scan rate of 0.1 V $s^{-1}$. The working electrode was a glass-carbon disk electrode. The counter electrode was a Pt wire. The reference electrode was $Ag/Ag^+$. A ferrocenium/ferrocene ($Fc^+/Fc$) redox couple was used as the internal standard. All potentials relative to $Ag/Ag^+$ electrode obtained from CV measurement were referenced against $Fc^+/Fc$ to calculate HOMO/LUMO levels. As a result, the $Ag/Ag^+$ electrode is just a pseudo-reference. The HOMO/LUMO levels are calculated according to the following formalism: $E_{HOMO}/E_{LUMO} = -(4.8+E_{OX}/E_{red})$; $\Delta E_g = E_{LUMO}-E_{HOMO}$.

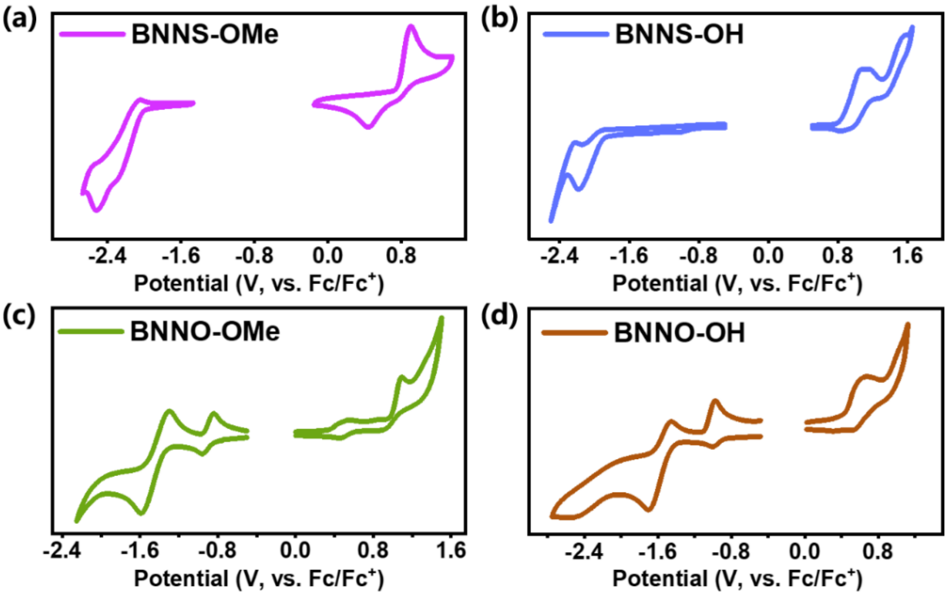


**Figure S12.** Cyclic voltammogram (CV) diagrams of (a) **BNNS-OMe**, (b) **BNNS-OH**, (c) **BNNO-OMe**, (d) **BNNO-OH**, showing the reduction (recorded in THF) and oxidation waves (recorded in DCM) vs Fc/Fc+, using n-$Bu_4NPF_6$ (0.1 M) as the electrolyte, ν = 100 mV/s.

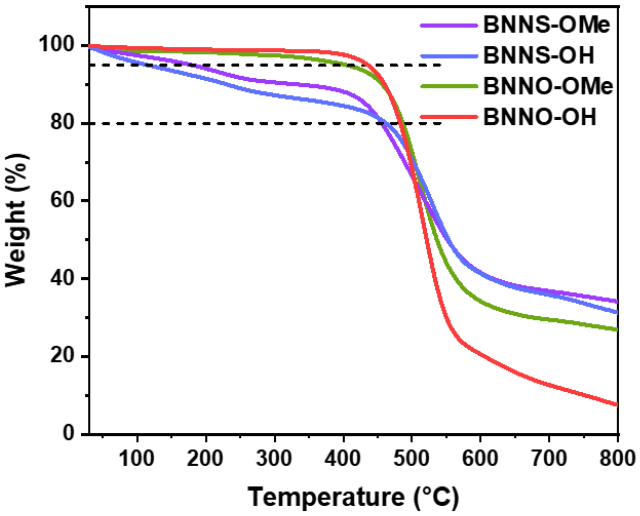


**Figure S13.** TGA traces for the compounds.

**Table S11.** Thermal stability data of the four molecules. (The decomposition temperature determined from the temperature at 5 wt% and 20 wt% loss.)

| **Compounds** | ***T$_d$* (5%)/°C** | ***T$_d$* (20%) /°C** |
|---|---|---|
| **BNNS-OMe** | 180 | 456 |
| **BNNS-OH** | 115 | 463 |
| **BNNO-OMe** | 405 | 487 |
| **BNNO-OH** | 436 | 483 |

## S7. Device fabrications and measurements

The indium tin oxide (ITO) glass substrates with a sheet resistance of 15 Ω per square were cleaned with optical detergent, deionized water, acetone and isopropanol successively, and then treated with plasma for 5 minutes. Subsequently, they were transferred to a vacuum chamber. Under high vacuum ($< 9 \times 10^{-5}$ Pa), the organic materials were deposited onto the ITO glass substrates at a rate of 0.6 Å $s^{-1}$. After finishing the deposition of organic layers, ITO glass substrates were patterned by a shadow mask with an array of 2.0 mm × 2.5 mm openings. Then LiF and Al were successively deposited at a rate of 0.2 Å $s^{-1}$ and 5 Å $s^{-1}$, respectively. The EL spectrum, CIE coordinate and luminance intensity of the OLEDs were recorded by Photo Research PR655, meanwhile, the current density ($J$) and driving voltage ($V$) were recorded by Keithley 2400. By assuming Lambertian distribution, the external quantum efficiency (EQE) was estimated according to brightness, electroluminescence spectrum and current density. The materials of device fabrication are provided by Jilin OLED Material Tech Co., Ltd.

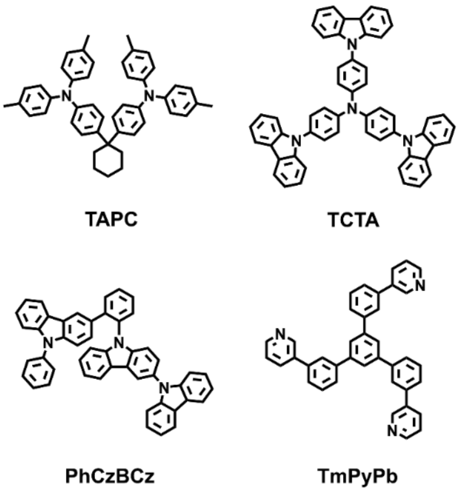


**Figure S14.** The chemical structures of all transport layers and host material in the doped devices.

# S8. NMR spectra

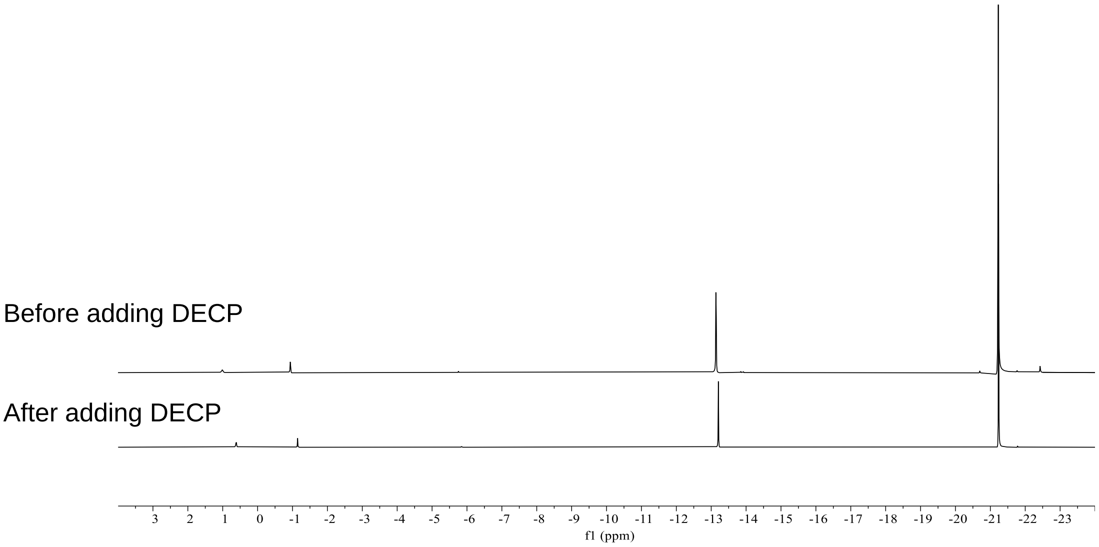


**Figure S15.** $^{31}$P NMR spectra of **BNNS-OMe** before and after adding DECP in $CDCl_3$ (202 MHz).

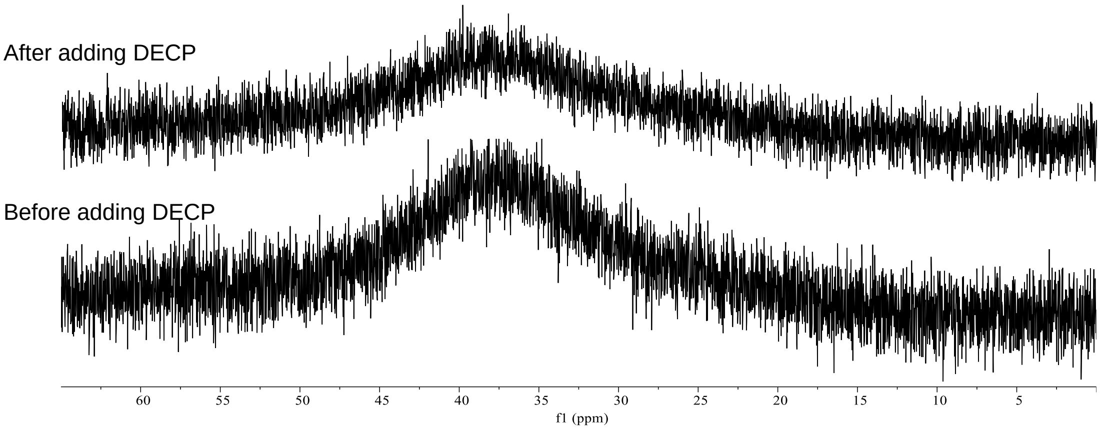


**Figure S16.** $^{11}$B NMR spectra of **BNNS-OMe** before and after adding DECP in $CDCl_3$ (160 MHz).

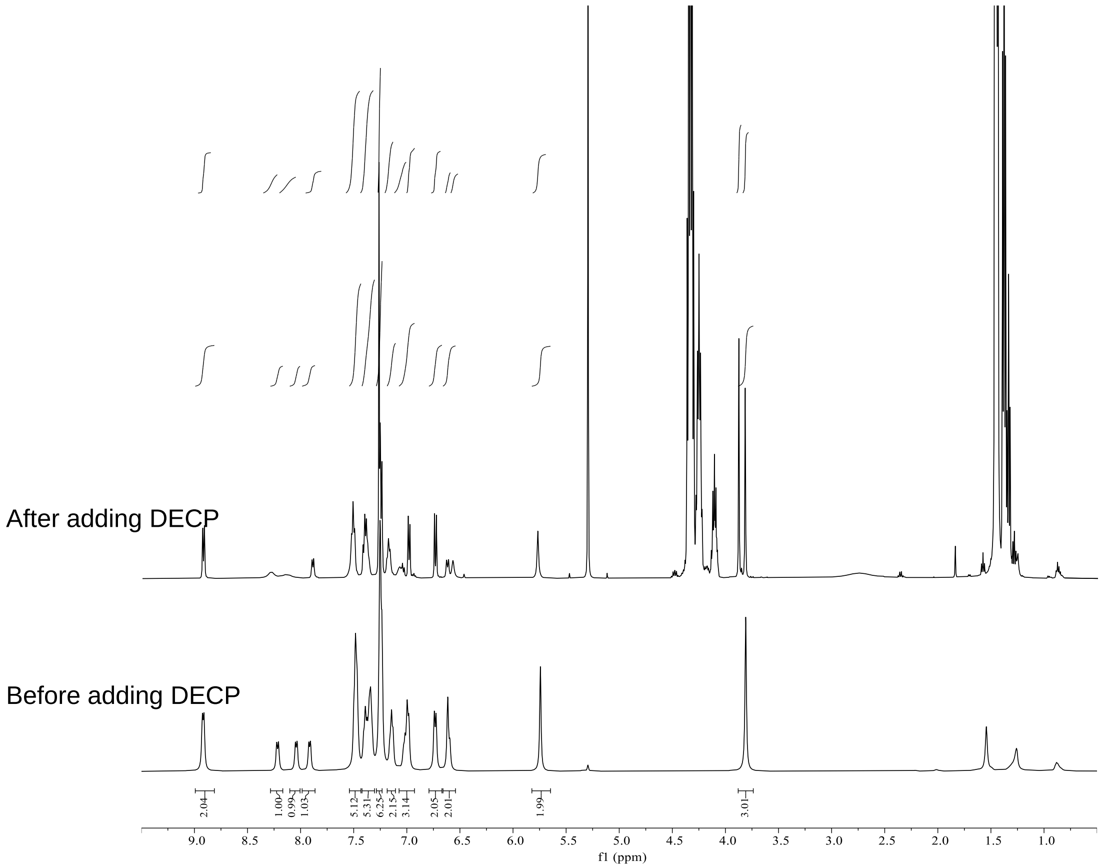


**Figure S17.** $^1$H NMR spectra of **BNNS-OMe** before and after adding DECP in $CDCl_3$ (500 MHz).

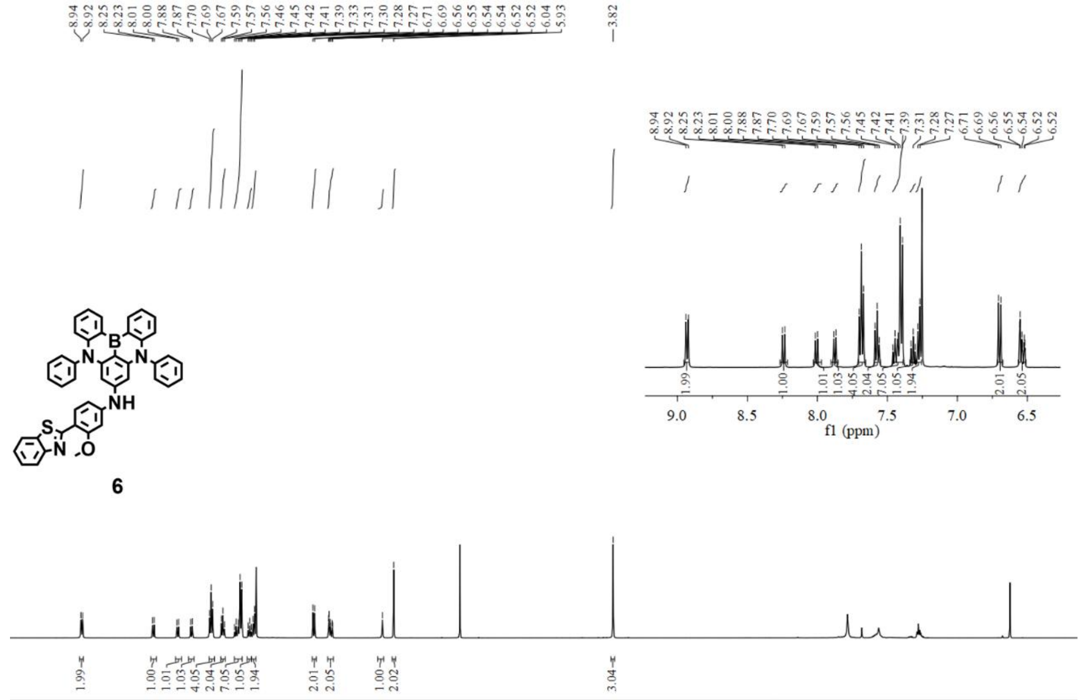


**Figure S18.** $^1$H NMR spectrum of **1** in $CDCl_3$ (500 MHz).

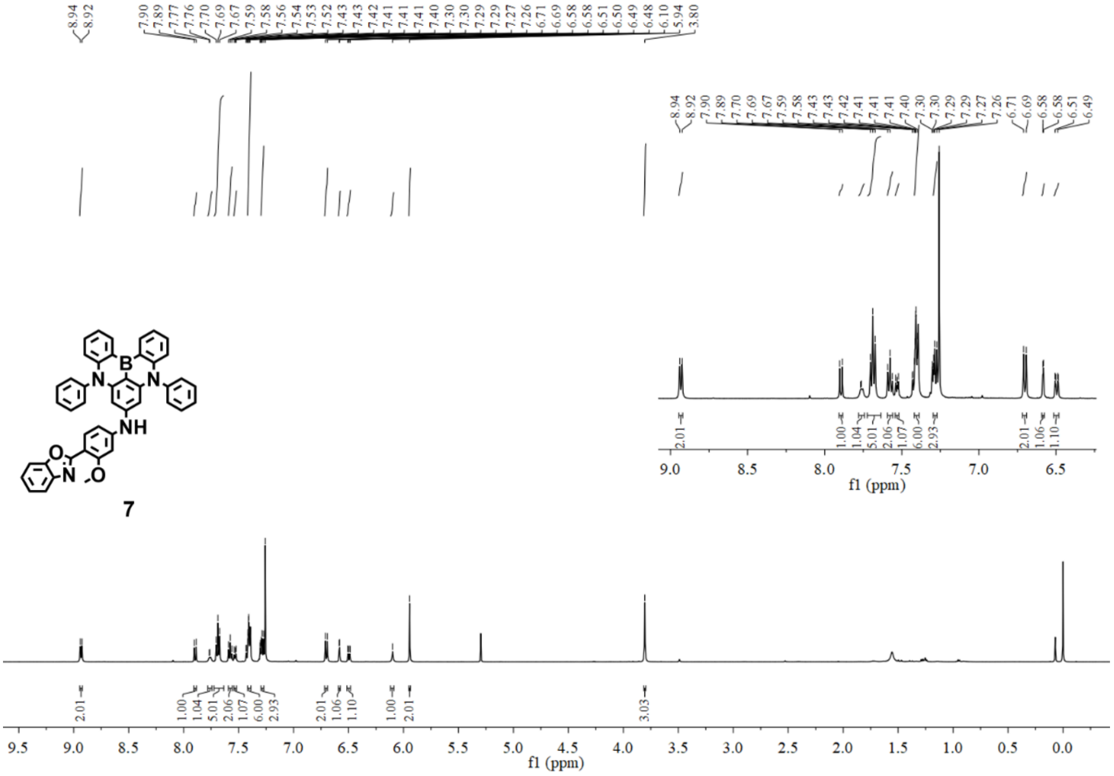


**Figure S19.** $^1$H NMR spectrum of **2** in $CDCl_3$ (500 MHz).

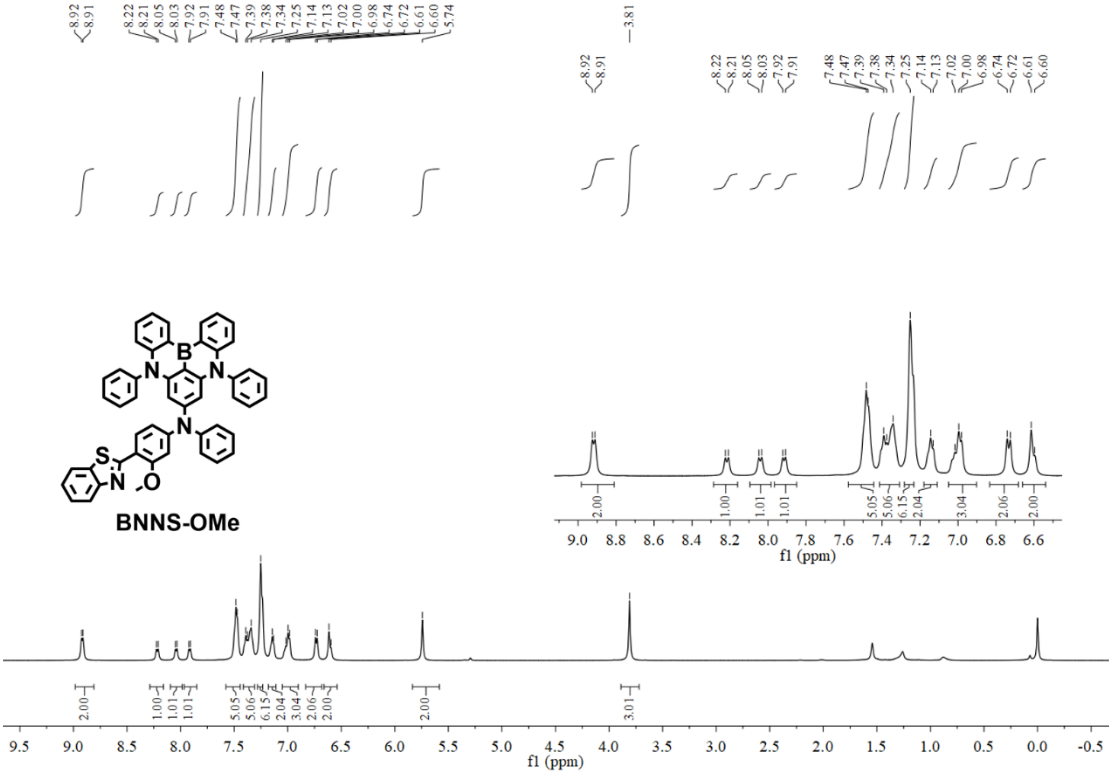


**Figure S20.** $^1$H NMR spectrum of **BNNS-OMe** in $CDCl_3$ (500 MHz).

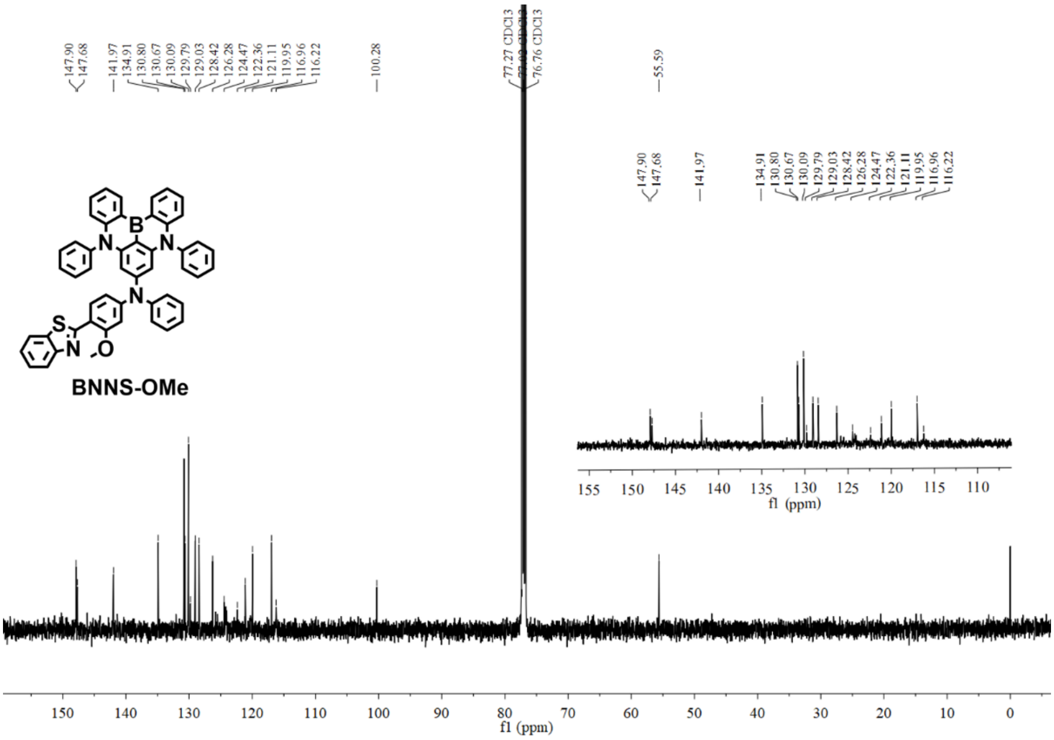


**Figure S21.** $^{13}$C NMR spectrum of **BNNS-OMe** in $CDCl_3$ (125 MHz).

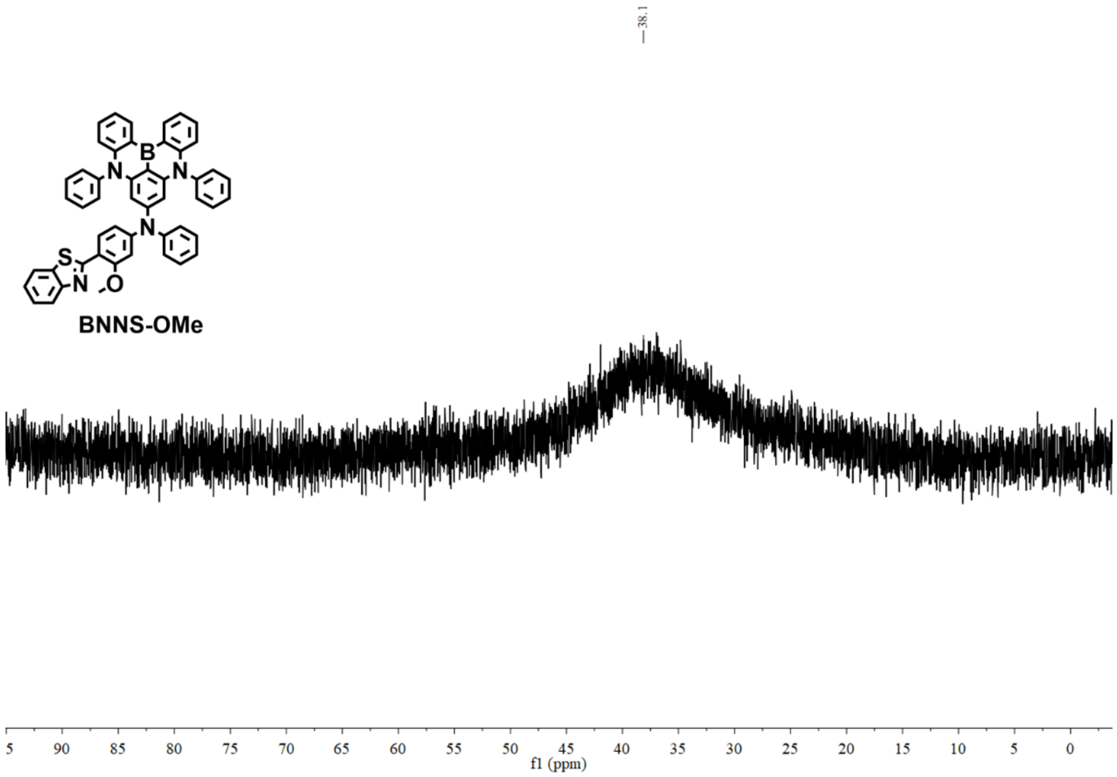


**Figure S22.** $^{11}$B NMR spectrum of **BNNS-OMe** in $CDCl_3$ (160 MHz).

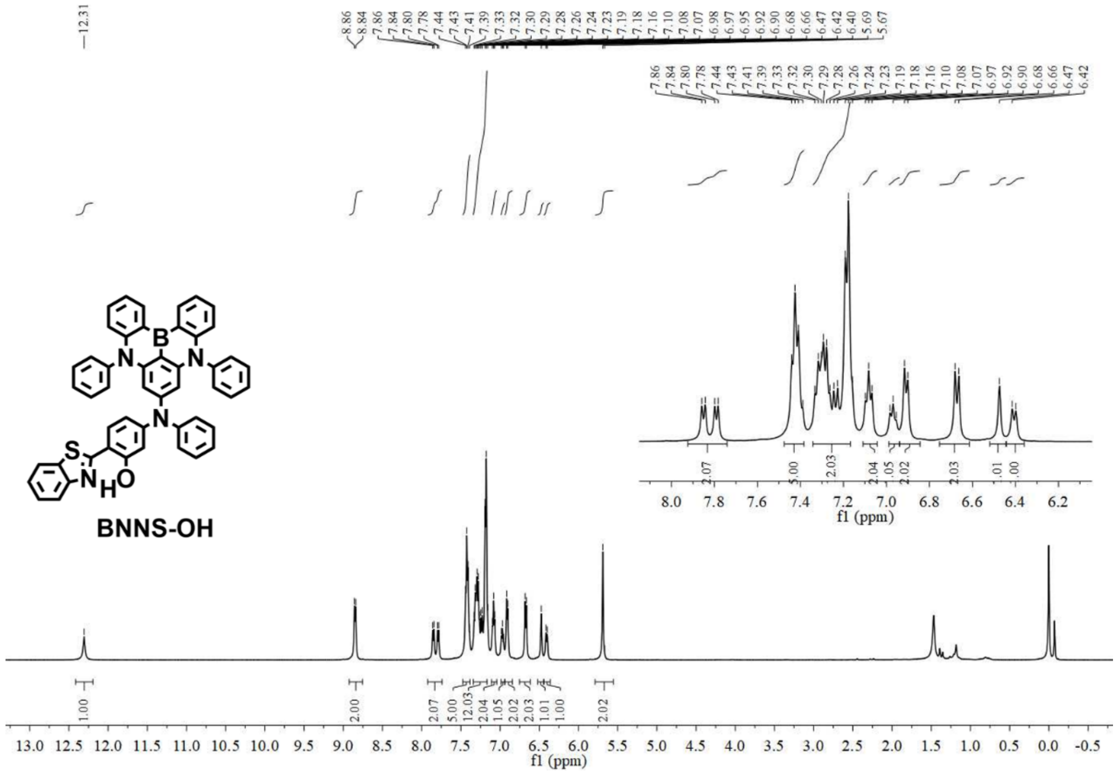


**Figure S23.** $^{1}$H NMR spectrum of **BNNS-OH** in $CDCl_3$ (500 MHz).

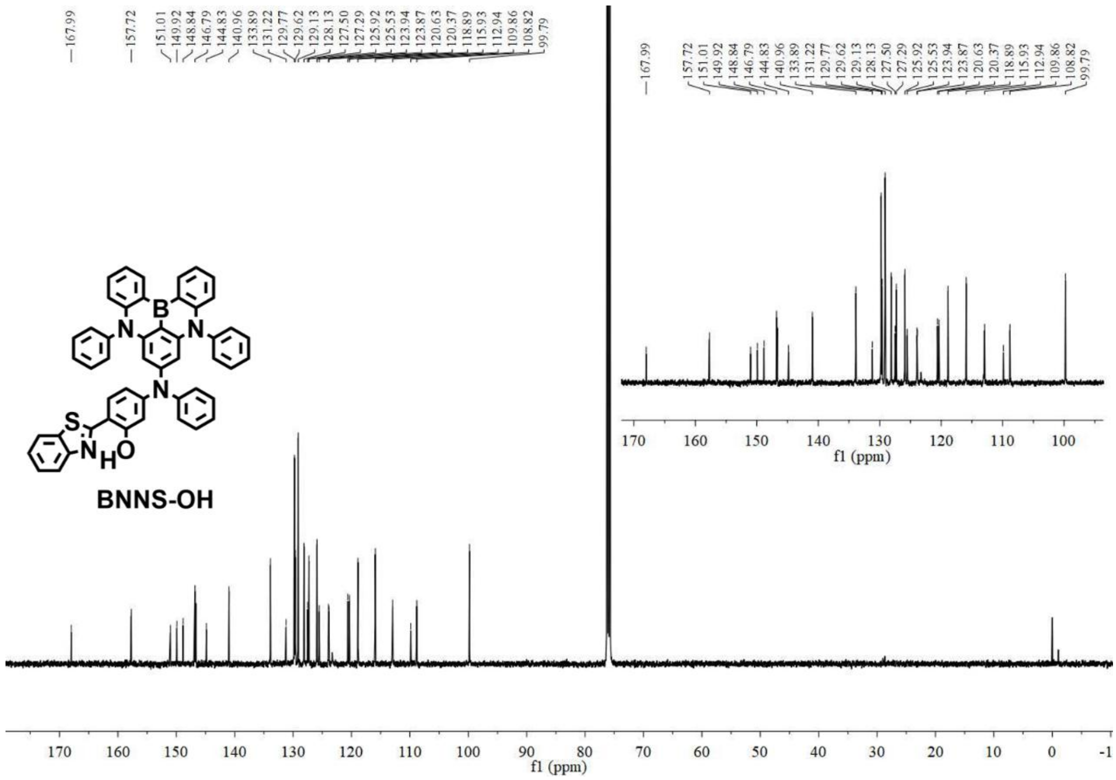


**Figure S24.** $^{13}$C NMR spectrum of **BNNS-OH** in CDCl$_3$ (125 MHz).

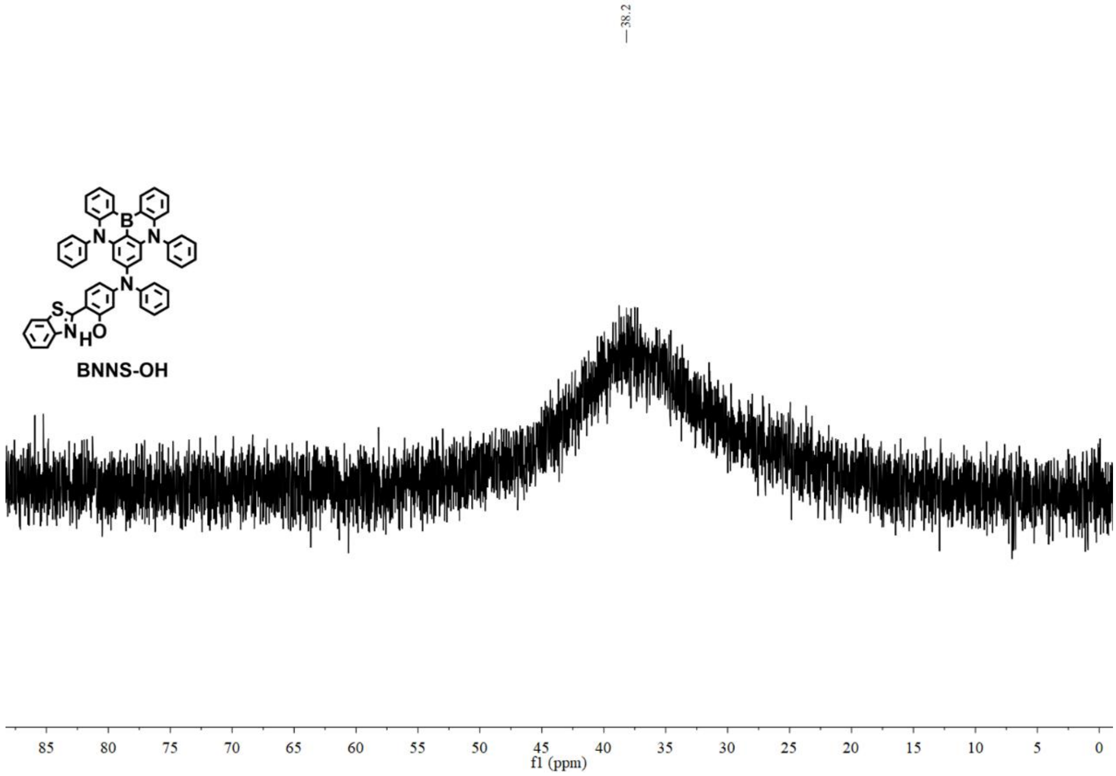


**Figure S25.** $^{11}$B NMR spectrum of **BNNS-OH** in CDCl$_3$ (160 MHz).

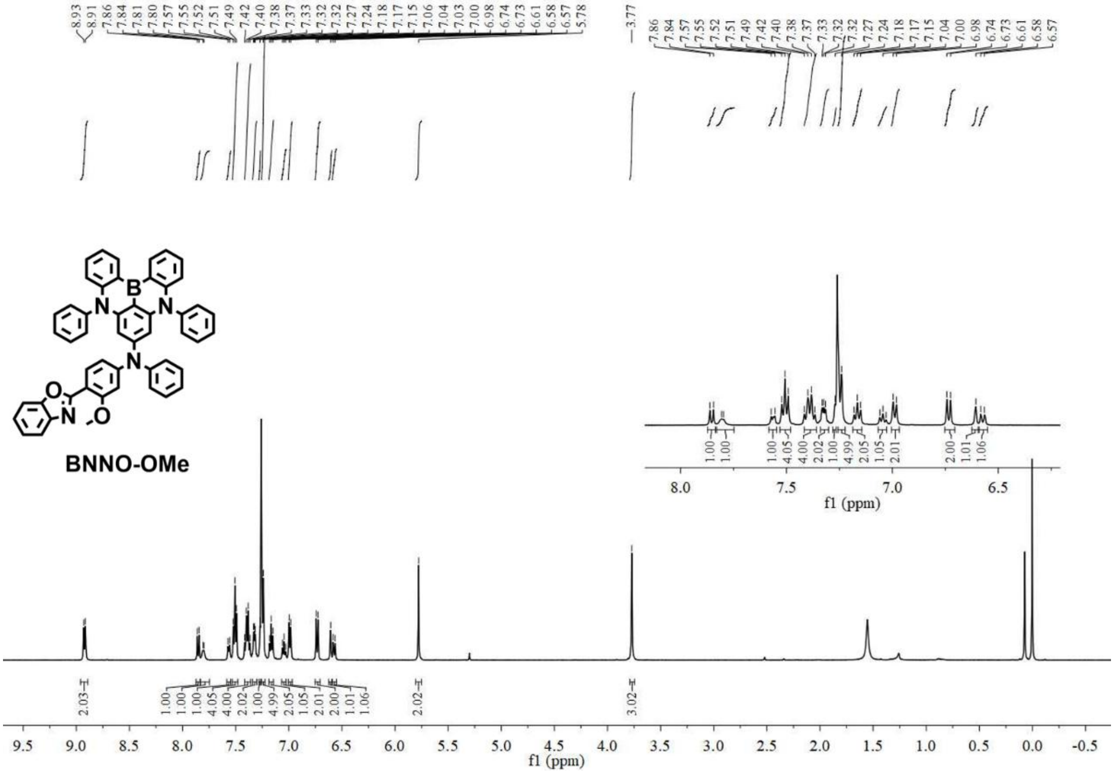


**Figure S26.** $^1$H NMR spectrum of **BNNO-OMe** in $CDCl_3$ (500 MHz).

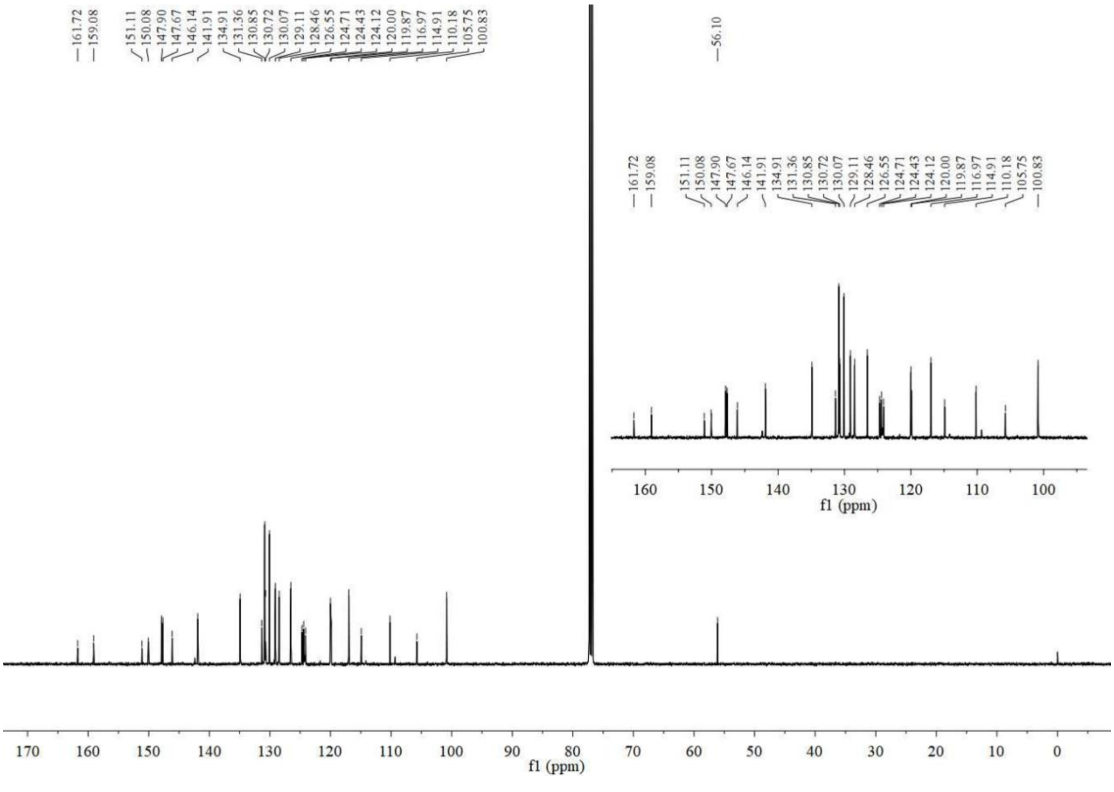


**Figure S27.** $^{13}$C NMR spectrum of **BNNO-OMe** in $CDCl_3$ (125 MHz).

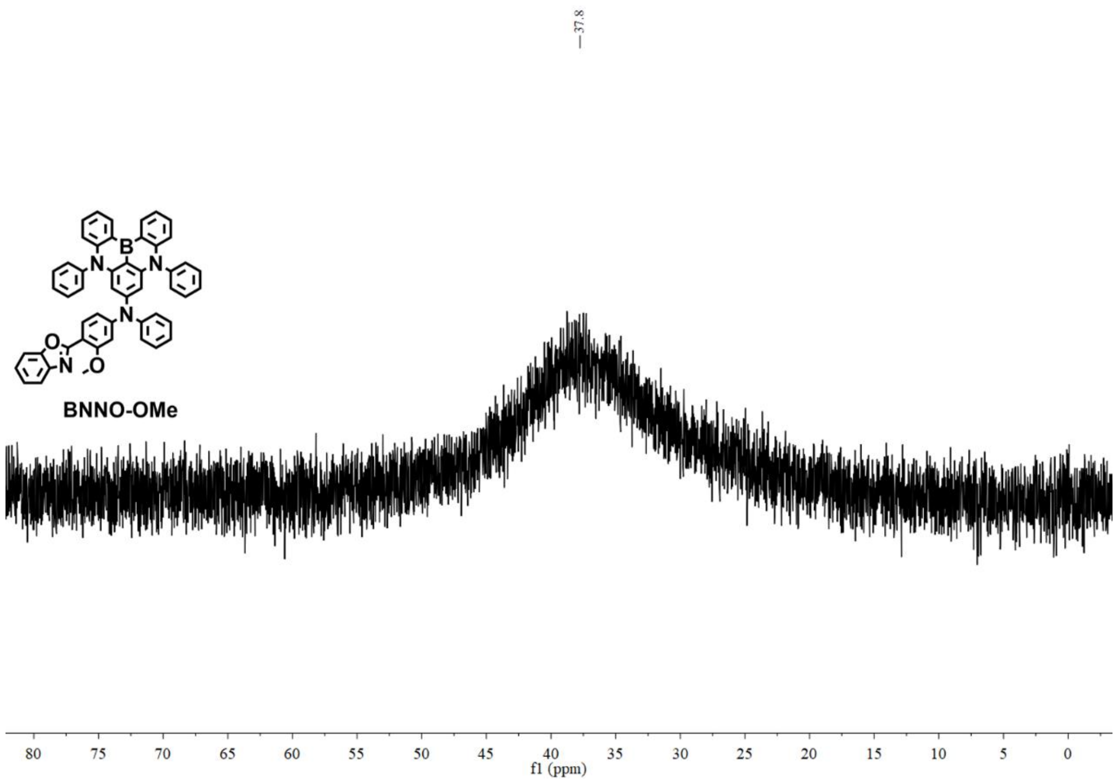


Figure S28. $^{11}$B NMR spectrum of **BNNO-OMe** in CDCl3 (160 MHz).

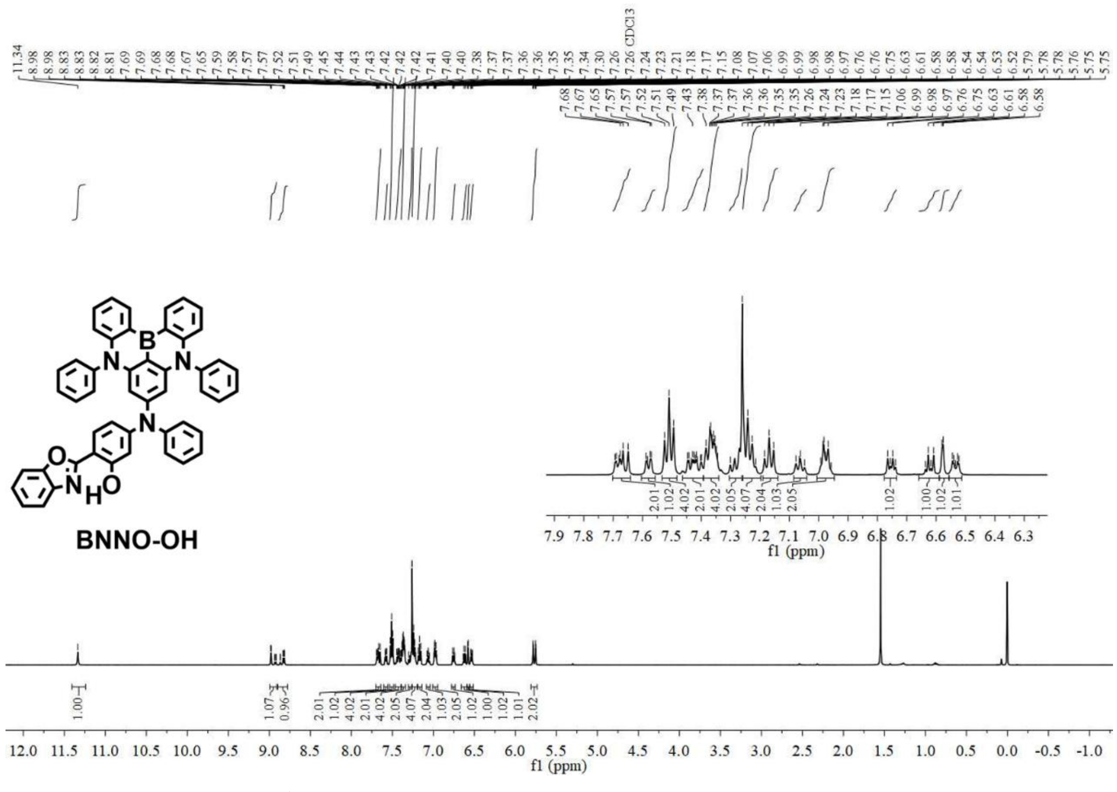


Figure S29. $^{1}$H NMR spectrum of **BNNO-OH** in CDCl3 (500 MHz).

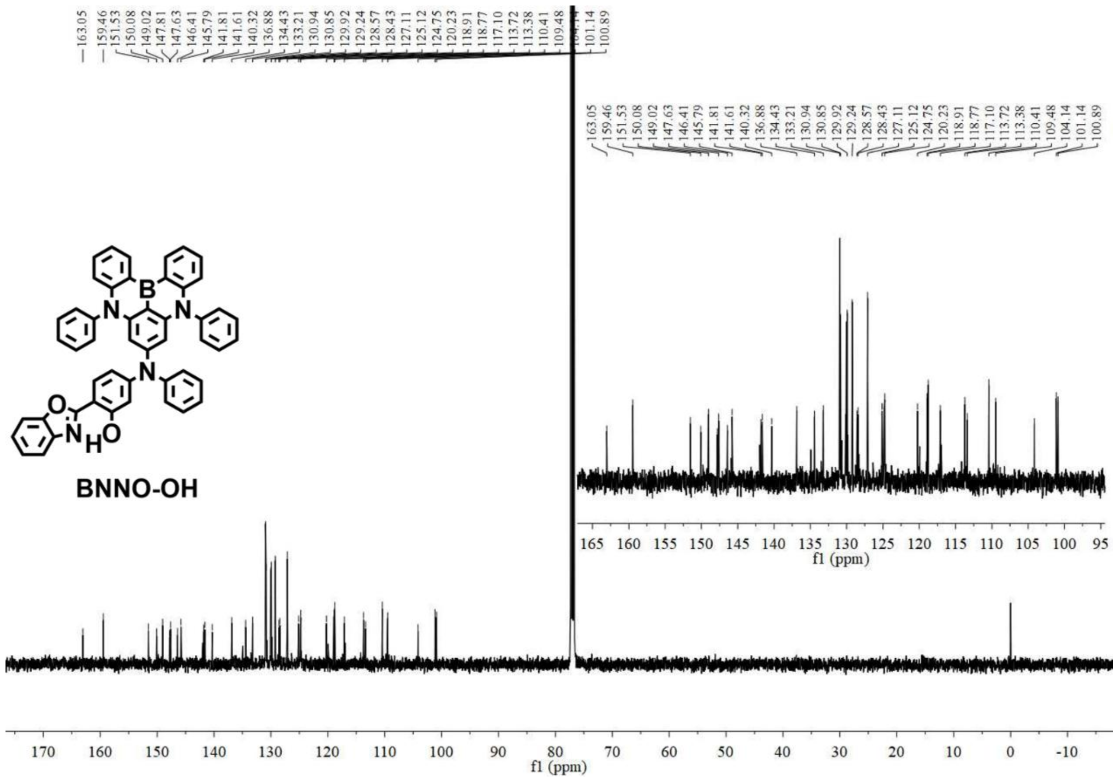


**Figure S30.** $^{13}$C NMR spectrum of **BNNO-OH** in $CDCl_3$ (125 MHz).

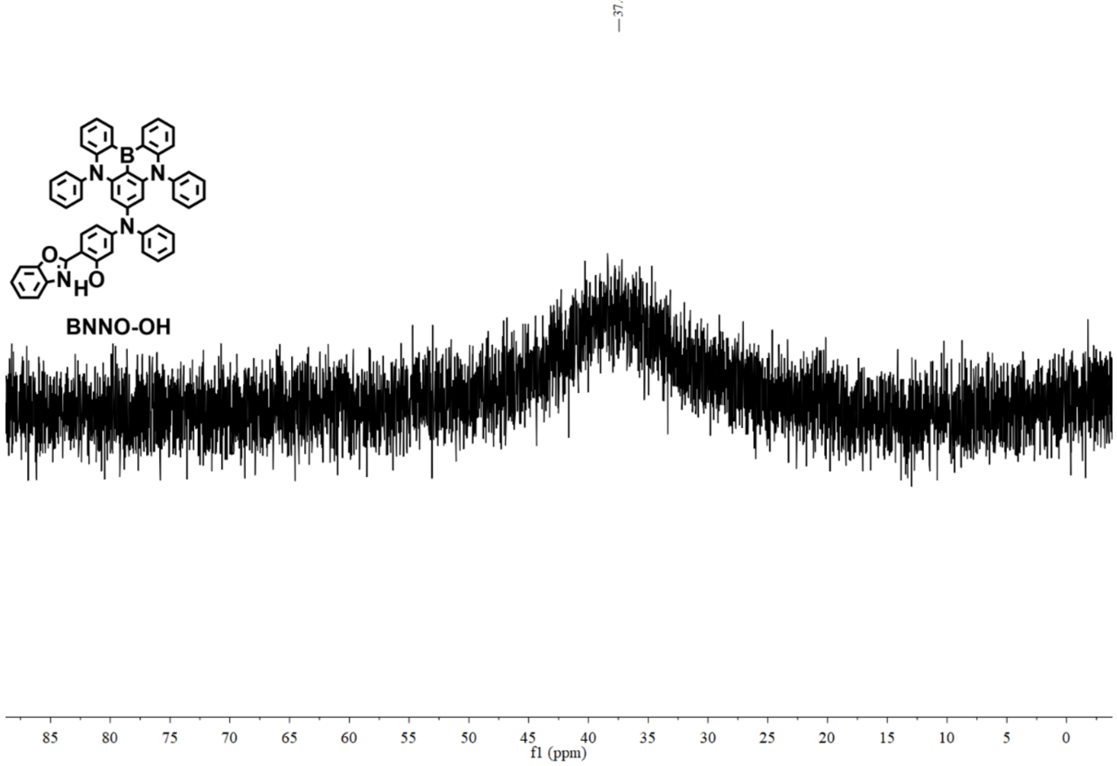


**Figure S31.** $^{11}$B NMR spectrum of **BNNO-OH** in $CDCl_3$ (160 MHz).

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