Supporting Information

Conformational Regulations to Realize Modifiable ESIPT (Excited-State Intramolecular Proton Transfer) by Intermolecular Interactions

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Experimental section

Physical measurements and instrumentation

All reaction materials were obtained from commercial suppliers and used without further purification. Absorption spectra in the UV−visible region were recorded with a Shimadzu UV−3600 spectrophotometer, in a 10×1 mm or 10×10 mm quartz cell. The photoluminescence spectra were measured on Edinburgh Instruments FS 5 and FLS 980 fluorescence spectrophotometers. Time-dependent single-photon counting technology (picosecond to microsecond) and multi-channel scanning technology (microsecond to second) were used for decay lifetime acquisition, using FLS 980 fluorescence spectrophotometer with 369.6 nm laser light source. The absolute photoluminescence quantum yields (PLQYs) were measured using a Hamamatsu C9920-02G absolute photoluminescence quantum yield measurement system.

Synthesis method and growth of single crystals

The parent molecule BDIBD was prepared according to our previous reports.
BDIBD is dissolved in hot DMF/MeOH (v/v 1/10), acetone and MeOH, respectively. After cooling to room temperature, the needle crystals of complex are obtained by filtration, and dried under a vacuum. Three crystals named BDIBD-DMF, BDIBD-ACE, BDIBD-MeOH were synthesized.

Crystal structure determination

Single−crystal diffraction data of molecules BDIBD-DMF, BDIBD-ACE and BDIBD-MeOH were collected on a Rigaku SuperNova X−ray diffractometer using micro−focus dual with X−ray Source of Cu–Kα radiation (λ = 1.54178 Å) at 240 K. Using Olex2, the structures were solved by SHELXT and refined using the full−matrix least−squares procedures within the SHELXTL software package. CCDC numbers **2169865**, **2402247, 2402248** contain the supplementary crystallographic data, and can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational Details

The density functional theory (DFT) was used to optimize the molecular structure in the ground state (S_0), while the geometry of the excited states was optimized with the time dependent density functional theory (TD-DFT). To provide the different ESIPT mechanisms in crystals, we used the ONIOM(QM/MM) approach with a two-layer model, combining the quantum mechanical (TD)-M06-2X/6-31G(d,p) with the universal force field (UFF) force field. The clusters for ONIOM calculations were cut from the X-ray single-crystal structure in the experiment. One BDIBD molecule was placed at the center of the model and treated at the QM level, which was optimized

without constraint. The surrounding molecules were computed by low-level UFF force field with QEQ charges and kept frozen during optimizations. High layer was completely surrounded by Low layer. From the chemical structure of BDIBD, we can deduce that there should be two ESIPT-related hydrogen bonds in BDIBD, and thus two proton transfer states may exist. The molecule without proton transfer is labeled as BDIBD-enol. The molecule with one proton transferred is named BDIBD-keto[1st]. The molecules with two protons transferred is called BDIBD-keto[2nd]. The IR vibrational frequencies are calculated at the same theoretical level as the geometric optimization, with no imaginary frequencies observed, thus confirming the accuracy of the optimization and the stability of the structure. The LUMO, HOMO and electron & hole maps of QM part calculated at the same level were performed using Multiwfn program and VMD program. The reduced density gradient (RDG) and the atoms in molecules topology analysis (AIM) were performed in the same level. Ab initio molecular dynamics (AIMD) was studied for simulated complexes changes performed at using PBE0/def2-SV(P) with RIJCOSX approximation employing ORCA 5.0.4 package. Natural adaptive orbitals (NAdO) of molecules obtained by AIMD were performed by Multiwfn program.
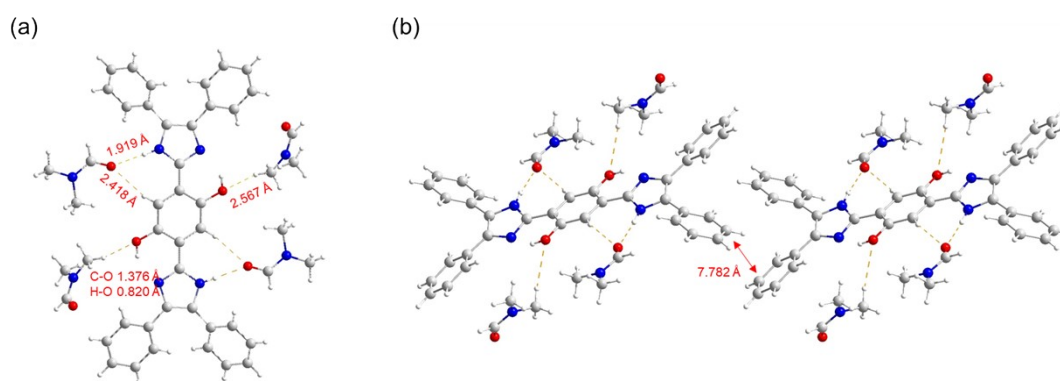

Figure S1 Crystal structure and packing diagrams of BDIBD-DMF.
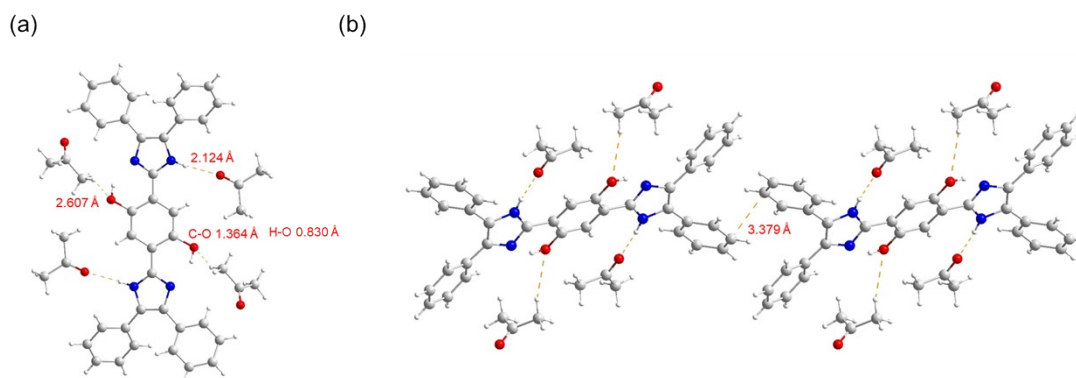
Figure S2 Crystal structure and packing diagrams of BDIBD-ACE.
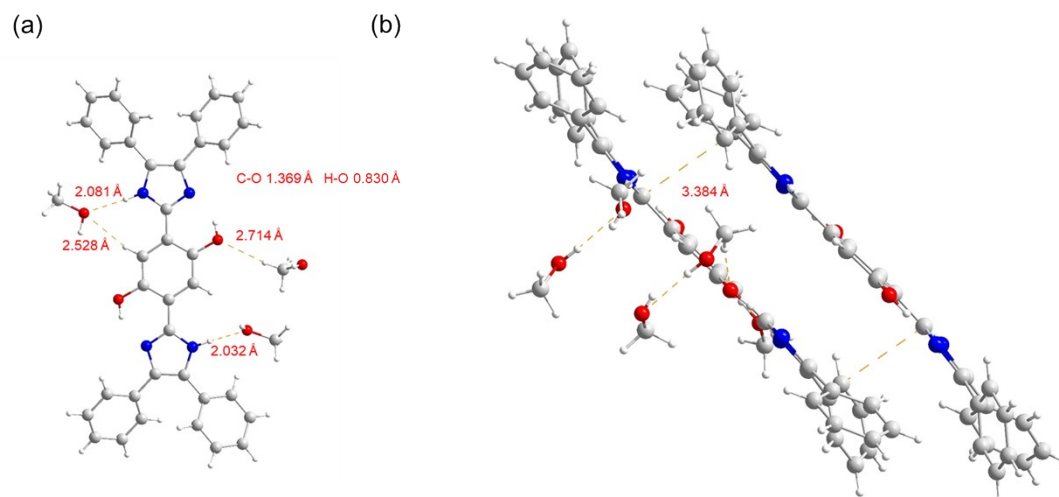
Figure S3 Crystal structure and packing diagrams of BDIBD-MeOH.
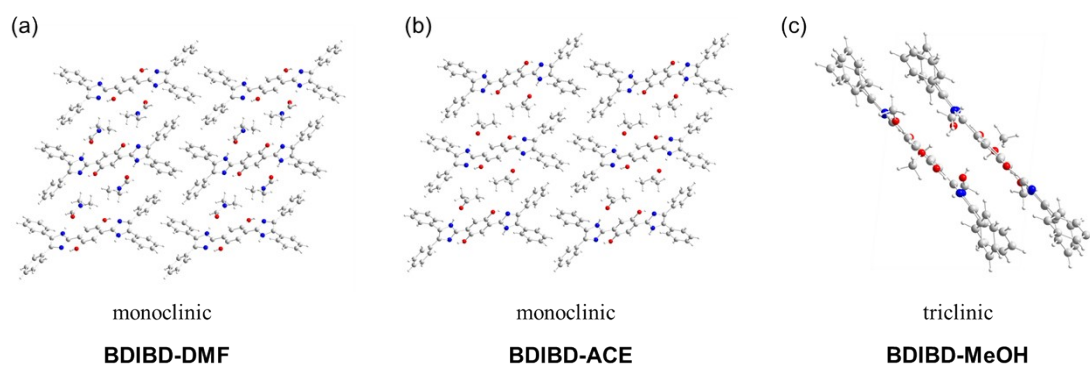
Figure S4 Crystal cells of (a) BDIBD-DMF, (b) BDIBD-ACE and (c) BDIBD-MeOH viewed from direction b, respectively.
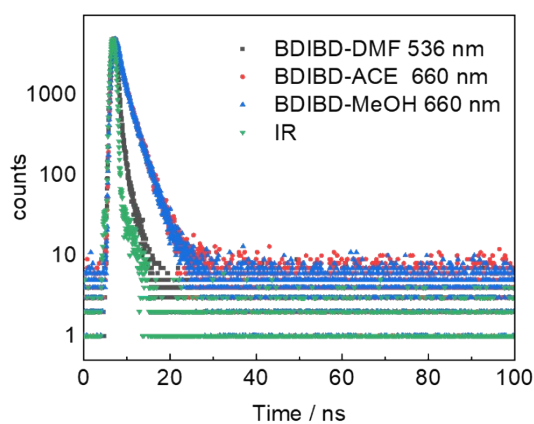
Figure S5 The luminescence decay lifetime of the crystals.
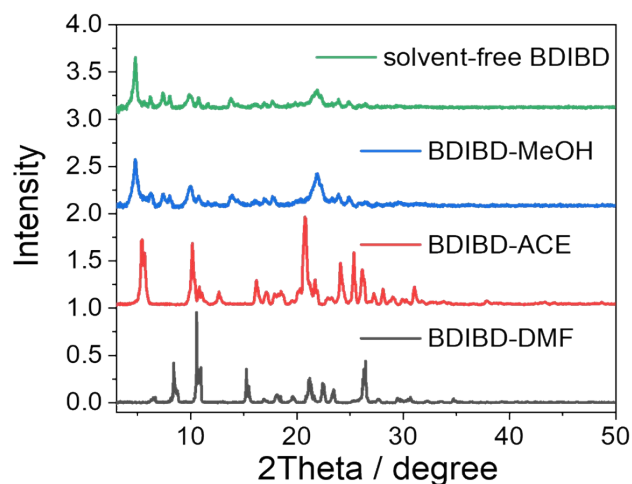
Figure S6 Powder X-ray diffraction pattern of BDIBD-DMF, BDIBD-ACE, BDIBD-MeOH and solvent-free BDIBD. The solvent-free BDIBD molecule is obtained by heating BDIBD-DMF at 100°C for 72 hours to remove the solvent.
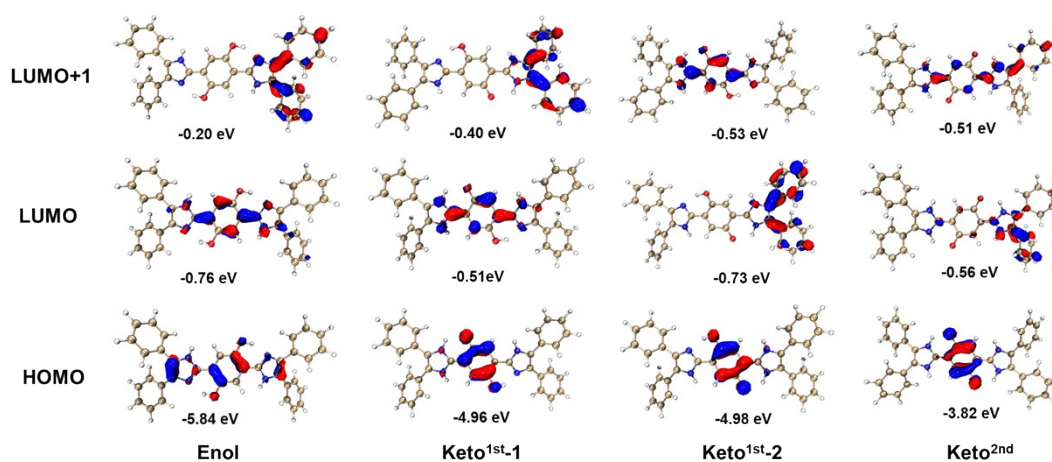
Figure S7 The frontier molecular orbitals of the QM part of BDIBD-DMF.
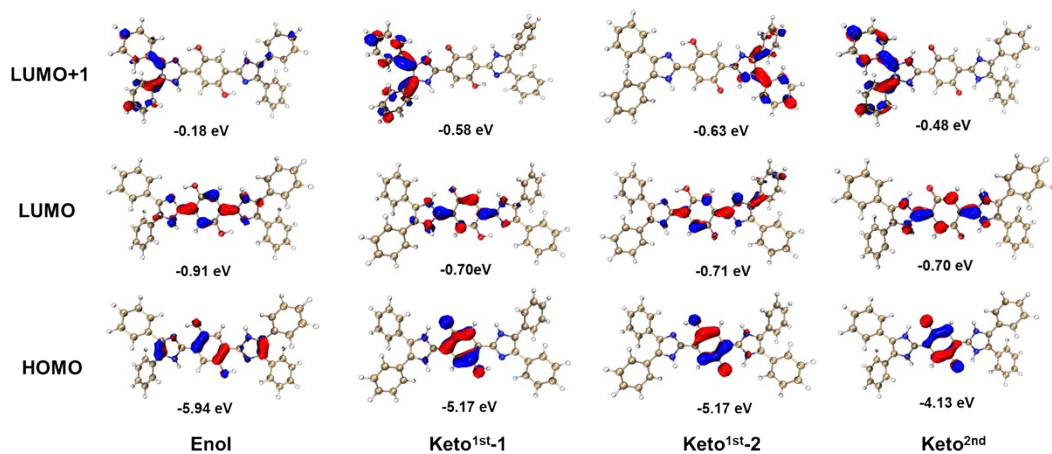
Figure S8 The frontier molecular orbitals of the QM part of BDIBD-ACE.
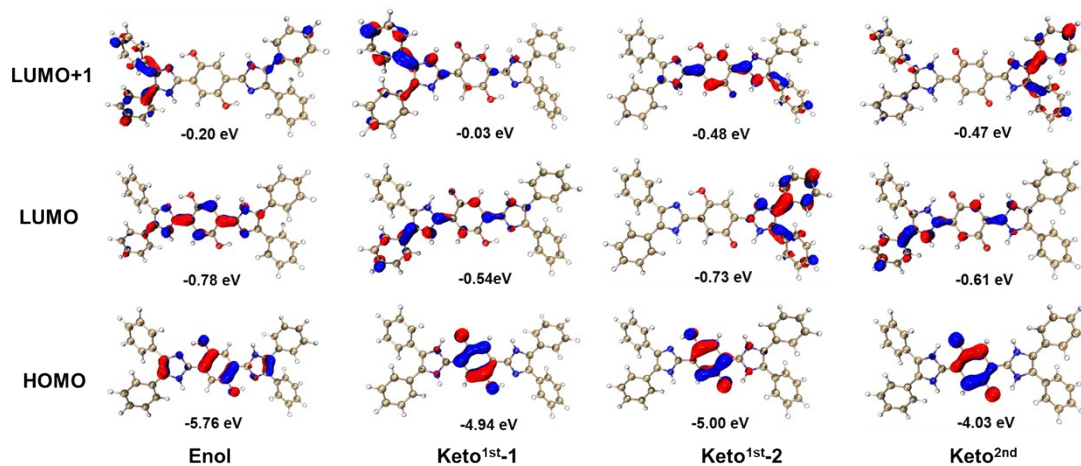
Figure S9 The frontier molecular orbitals of the QM part of BDIBD-MeOH.
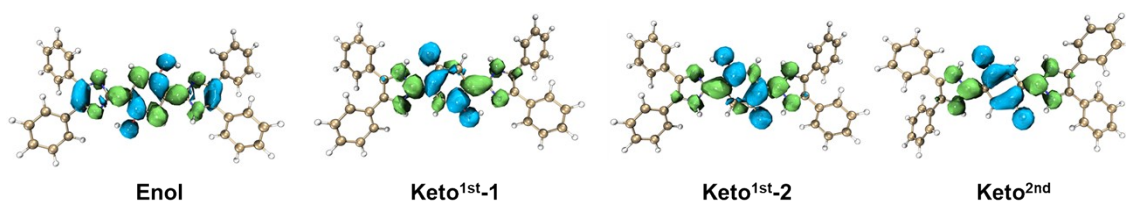
Figure S10 Calculated charge-density difference (CCD) between S_0 and S_1 states of the QM part of BDIBD-ACE with the blue and the green regions denoting the hole and electron distributions, respectively.
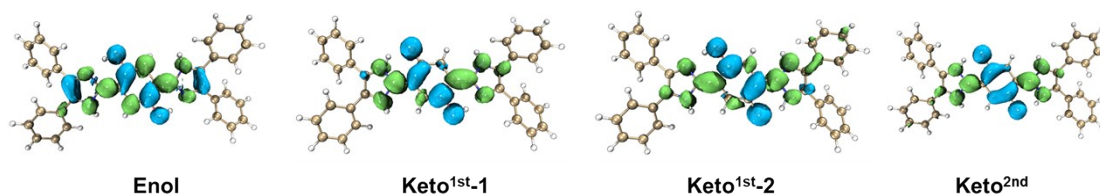
Figure S11 Calculated charge-density difference (CCD) between S_0 and S_1 states of the QM part of BDIBD-MeOH with the blue and the green regions denoting the hole and electron distributions, respectively.
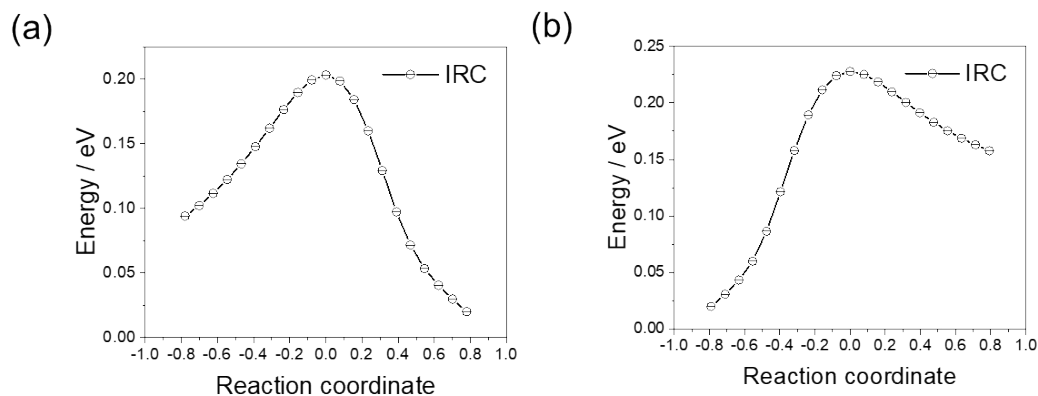
Figure S12 Calculated relative energy profile along the excited state IRC for BDIBD-ACE based on ONIOM-EE(TD-M06-2X/6-31G(d,p):UFF) level. (a) Path from enol to keto[1st]; (b) Path from keto[1st] to keto[2nd].
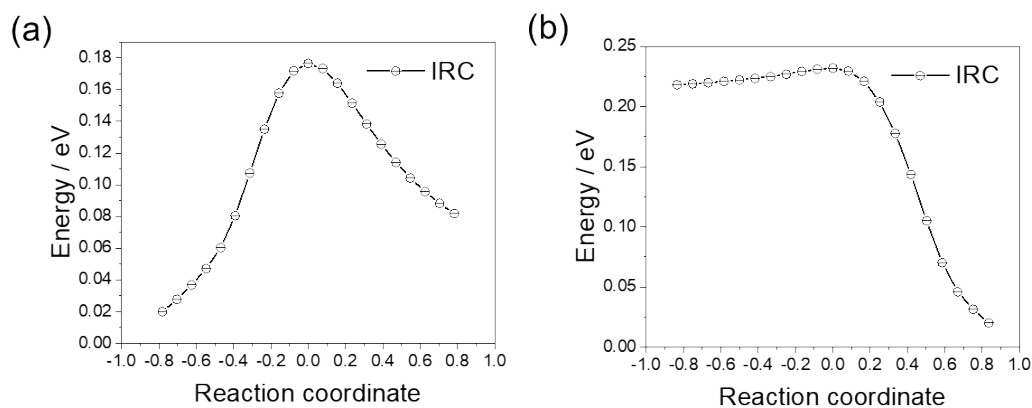
Figure S13 Calculated relative energy profile along the excited state IRC for BDIBD-MeOH based on ONIOM-EE(TD-M06-2X/6-31G(d,p):UFF) level. (a) Path from enol to keto[1st]; (b) Path from keto[1st] to keto[2nd].
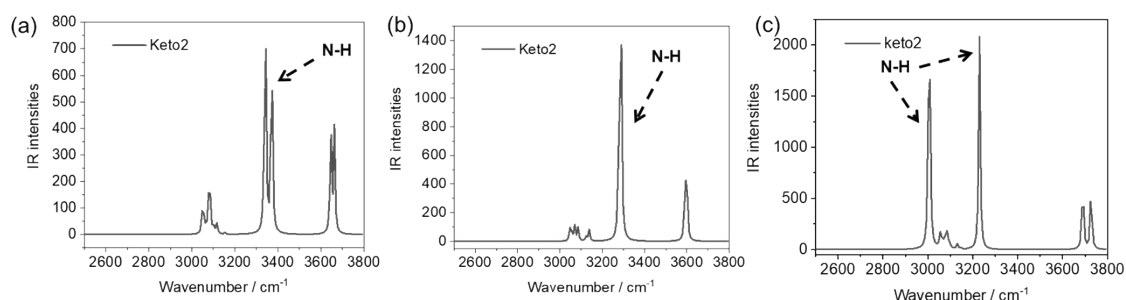
Figure S14 Simulated IR vibrational spectra of N–H formed by proton transfer synergetic stretching mode for (a) BDIBD-DMF, (b) BDIBD-ACE and (c) BDIBD-MeOH compounds in S_1 state, respectively.
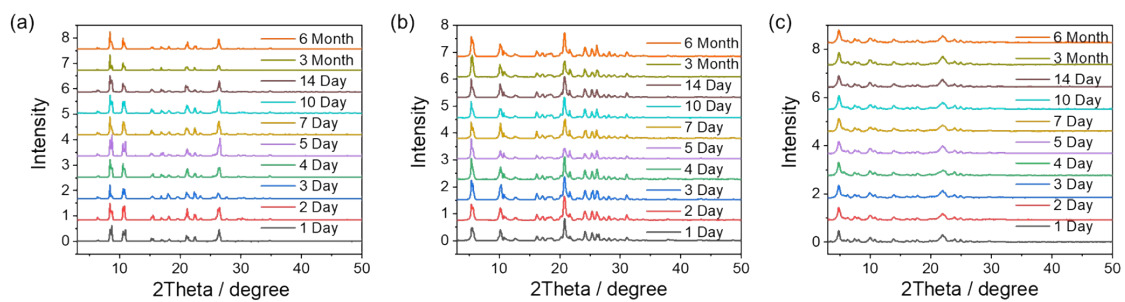
Figure S15 Time-dependent powder X-ray diffraction pattern of (a) BDIBD-DMF, (b) BDIBD-ACE, (c) BDIBD-MeOH under ambient conditions.

Table S1 Crystal data and structure refinement for crystals BDIBD-DMF, BDIBD-ACE and BDIBD-MeOH.

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
Empirical formula	$C_{21}H_{20}N_3O_2$	$C_{21}H_{19}O_2N_2$	$C_{39}H_{38}N_4O_5$
Formula weight	346.40	341.39	628.71
Temperature/K	240.00(10)	249.96(13)	250.00(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C2/c*	*C2/c*	*P-1*
a/Å	33.779(8)	34.052(3)	9.7843(9)
b/Å	5.9722(10)	5.8249(6)	11.0773(12)
c/Å	17.985(4)	17.723(2)	15.682(2)
α/°	90	90	99.283(10)
β/°	103.99(3)	102.677(10)	95.760(9)
γ/°	90	90	93.226(8)
Volume/Å^3	3520.6(14)	3429.7(6)	1664.4(3)
Z	8	8	2
ρcalcg/cm^3	1.307	1.322	1.255
μ/mm^{-1}	0.688	0.667	0.632
F(000)	1464.0	1440.0	660.0
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.138 to 147.008	10.232 to 101.578	8.11 to 101.1
Reflections collected	5531	10121	7876
Independent reflections	3385	1796	3462
	R_{int} = 0.0586, R_{sigma} = 0.1028	R_{int} = 0.0537, R_{sigma} = 0.0385	R_{int} = 0.0592, R_{sigma} = 0.0881
Data/restraints/parameters	3385/0/238	1796/0/230	3462/0/447
Goodness-of-fit on F^2	1.064	1.067	0.935
Final R indexes [I≥2σ (I)]	R1 = 0.0808, wR2 = 0.2058	R1 = 0.0473, wR2 = 0.1225	R1 = 0.0627, wR2 = 0.1602
Final R indexes [all data]	R1 = 0.1280, wR2 = 0.2675	R1 = 0.0589, wR2 = 0.1355	R1 = 0.0980, wR2 = 0.1988
Diff. peak/hole/e Å^{-3}	0.27/-0.35	0.17/-0.22	0.29/-0.27

Table S2 Selected bond lengths (Å) for molecules with estimated standard deviations (e.s.d.s.) in parentheses.

BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
N1-C15	N11-C10	N3-C1
1.358	1.352	1.355
N2-C15	N9-C10	N5-C1
1.347	1.322	1.324
N1-C7	N11-C7	N3-C11
1.389	1.381	1.386
N2-C8	N9-C8	N3-C12
1.395	1.393	1.382
C7-C8	C7-C8	C11-C12
1.376	1.368	1.377
O1-N1	O21-N9	O1-N5
2.786	2.622	1.566

Table S3 Selected bond angles (°) and dihedral angles (°) for molecules with estimated standard deviations (e.s.d.s.) in parentheses.

BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
N1-C15-N2	N11-C10-N9	N3-C1-N5
110.4	110.4	110.6
C15-N1-C7	C10-N11-C7	C1-N3-C11
108.8	108.3	108.0
C15-N2-C8	C10-N9-C8	C1-N5-C12
105.4	106.5	106.7
N1-C7-C8	N11-C7-C8	N3-C11-C12
105.0	105.6	109.3
N2-C8-C7	N9-C8-C7	N5-C12-C11
110.5	109.1	105.4
N2-C8-C9-C14	N9-C8-C1-C2	N6-C16-C19-C13

26.1	23.8	34.7
N2-C8-C9-C10	N9-C8-C1-C6	N6-C16-C19-C26
-150.5	-152.0	-145.8
N1-C7-C6-C5	N11-C7-C12-C17	N4-C12-C11-C20
133.3	135.6	141.987
N1-C7-C6-C1	N11-C7-C12-C13	N4-C12-C11-C22
-43.0	-40.8	-37.7
N2-C15-C16-C18	N11-C10-C18-C20	N4-C4-C7-C8
-12.5	-13.8	-4.5
N1-C15-C16-C17	N9-C10-C18-C19	N4-C4-C7-C14
14.8	14.0	5.8

Table S4 Bond lengths of O-H bond, O-N bond, intramolecular hydrogen bond and bond angles (°) in each ligand and coordination polymer.

Sample	O-H (Å)	O-N (Å)	O-H···N (Å)	O-H···N (°)
BDIBD-DMF	0.820	2.643	1.916	147.262
BDIBD-ACE	0.830	2.622	1.880	148.164
BDIBD-MeOH	0.830	2.566	1.820	148.709

Table S5 Data summary of the decay lifetime for ESIPT crystals in solid state (λ_{ex} = 369.6 nm).

Lifetime / ns	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
	0.727	1.919	1.881

Table S6 Data summary of photoluminescence quantum yield (PLQY) for ESIPT crystals in solid state.

PLQY	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
	0.091	0.068	0.078

Table S7 The relative Keto[1st] and Keto[2ed] energy (eV) of BDIBD-DMF calculated by different kind of functionals.

Method	Keto[1st]	Keto[2ed]
M06-2X	0.05	0.36
CAM-B3LYP	-0.03	0.16
PBE0	-0.43	-0.22
ωB97XD	-0.06	0.12

Table S8 The relative Keto[1st] and Keto[2ed] energy (eV) of BDIBD-ACE calculated by different kind of functionals.

Method	Keto[1st]	Keto[2ed]
M06-2X	0.07	0.24
CAM-B3LYP	0.01	0.07
PBE0	-0.33	-0.26
ωB97XD	-0.07	0.01

Table S9 The relative Keto[1st] and Keto[2ed] energy (eV) of BDIBD-MeOH calculated by different kind of functionals.

Method	Keto[1st]	Keto[2ed]
M06-2X	0.05	0.29
CAM-B3LYP	-0.03	0.13
PBE0	-0.51	-0.39
ωB97XD	-0.06	0.08

Table S10 The key geometry parameters and relative energies (nm) of BDIBD-DMF calculated by different kind of functionals.

Method	Absorbance	Emission		
		Enol	Keto[1st]-1	Keto[2ed]
Experiment	360	-	536	-
M06-2X	324	378	494	791
CAM-B3LYP	329	384	490	719
PBE0	364	425	771	1505
ωB97XD	326	379	487	717

Table S11 The key geometry parameters and relative energies (nm) of BDIBD-ACE calculated by different kind of functionals.

Method	Absorbance	Emission		
		Enol	Keto[1st]-1	Keto[2ed]
Experiment	360	-	522	660
M06-2X	331	385	485	725
CAM-B3LYP	331	385	490	719
PBE0	338	385	771	1505
ωB97XD	330	385	487	717

Table S12 The key geometry parameters and relative energies (nm) of BDIBD-MeOH calculated by different kind of functionals.

Method	Absorbance	Emission		
		Enol	Keto[1st]-1	Keto[2ed]
Experiment	360	-	-	636
M06-2X	340	390	482	698
CAM-B3LYP	329	396	484	692
PBE0	390	438	902	1778
ωB97XD	342	391	481	695

Table S13 Absorbance wavelengths and oscillator strength calculated for BDIBD-DMF.

State	Energy (eV)	Absorption (nm)	oscillator strength	Transition configuration
S_1	3.8241	324.22	1.1104	H→L (75.3%)
				H→L+1 (11.0%)
				H-1→L (4.2%)
S_2	4.3809	283.01	0.1723	H→L+1 (40.0%)
				H-2→L (25.4%)
				H-1→L+1 (13.8%)
				H→L (8.1%)
				H-2→L+1 (6.8%)
S_3	4.4735	277.15	0.1569	H→L+2 (31.9%)
				H-1→L (23.5%)
				H-1→L+2 (9.4%)
				H-2→L (8.9%)
				H→L+1 (8.9%)
S_4	4.6158	268.61	0.6321	H→L+2 (37.8%)
				H-2→L (16.0%)
				H-1→L+2 (11.8%)
				H-1→L (11.6%)
				H-2→L+1 (8.6%)

Table S14 Emission wavelengths and oscillator strength calculated for BDIBD-DMF-enol.

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	3.2760	378.46	1.3010	H→L (89.9%)
				H→L+1 (2.5%)
S_2	4.0531	305.90	0.1427	H→L+1 (44.2%)
				H-2→L (31.3%)
				H-1→L+1 (12.0%)
				H-2→L+1 (3.3%)
				H→L (3.2%)
S_3	4.1205	300.89	0.1614	H-1→L (32.3%)
				H→L+1 (22.2%)
				H-2→L (18.3%)
				H→L+2 (11.0%)
				H-2→L+1 (5.1%)
				H-1→L+2 (3.6%)
S_4	4.2789	289.76	0.5068	H→L+2 (64.2%)
				H-1→L+2 (12.9%)
				H-2→L (10.5%)

H-2→L+1 (2.2%)

Table S15 Emission wavelengths and oscillator strength calculated for BDIBD-DMF-keto[1st].

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	2.5091	494.14	0.4487	H→L (94.6%)
				H→L+2 (3.2%)
S_2	3.1728	390.77	0.0436	H→L+1 (97.8%)
S_3	3.7604	329.71	0.0139	H→L+2 (88.0%)
				H→L (3.8%)
				H-3→L (3.5%)
S_4	3.8369	323.14	0.0810	H-3→L (64.9%)
				H-2→L+2 (15.7%)
				H→L+2 (5.3%)
				H-3→L+2 (3.9%)
				H-3→L+10 (2.3%)

Table S16 Emission wavelengths and oscillator strength calculated for BDIBD-DMF-keto[2nd].

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	1.5678	790.83	0.2859	H→L+1 (80.6%)
				H→L (20.6%)
S_2	2.0036	618.80	0.0092	H→L (78.9%)
				H→L+1 (20.1%)
S_3	2.3518	527.19	0.0106	H→L+2 (99.0%)
S_4	2.9966	413.75	0.0006	H→L+3 (99.4%)

Table S17 Absorbance wavelengths and oscillator strength calculated for BDIBD-ACE.

State	Energy (eV)	Absorption (nm)	oscillator strength	Transition configuration
S_1	3.7453	331.04	1.1506	H→L (85.9%)
				H-2→L (4.5%)
				H→L+2 (3.1%)
S_2	4.4114	281.06	0.287	H-2→L (36.5%)
				H→L+2 (19.4%)
				H-1→L+1 (18.0%)
				H→L+1 (13.6%)
				H→L (4.9%)
S_3	4.4244	280.23	0.0360	H→L+1 (45.5%)
				H-1→L+2 (16.7%)
				H-1→L (14.4%)
				H→L+2 (11.6%)
				H-2→L+1 (3.9%)
				H-2→L (3.8%)
S_4	4.5875	270.27	0.6419	H-2→L (35.5%)
				H→L+2 (33.1%)
				H-1→L+1 (8.3%)
				H-2→L+1 (7.2%)
				H→L+9 (3.2%)

Table S18 Emission wavelengths and oscillator strength calculated for BDIBD-ACE-enol.

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	3.2212	384.91	1.2949	H→L (92.0%)
				H-2→L (2.6%)
S_2	4.0838	303.60	0.2688	H-2→L (66.8%)
				H→L+2 (13.2%)
				H-1→L+1 (7.2%)
				H→L (3.1%)
				H→L+9 (2.2%)
S_3	4.1373	299.68	0.0035	H→L+1 (65.9%)
				H-1→L (12.9%)
				H-1→L+2 (12.5%)
				H-2→L+1 (3.1%)
				H→L+2 (2.3%)
S_4	4.2620	290.91	0.5770	H→L+2 (58.5%)
				H-2→L (17.1%)

H-1→L+1 (11.5%)

H-2→L+2 (3.6%)

Table S19 Emission wavelengths and oscillator strength calculated for BDIBD-ACE-keto[1st].

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	2.5573	484.82	0.4970	H→L (90.7%)
				H→L+1 (6.1%)
S_2	3.1962	387.91	0.0462	H→L+1 (91.3%)
				H→L (6.3%)
S_3	3.9485	314.00	0.1988	H-3→L (58.7%)
				H-1→L (10.6%)
				H→L+2 (10.3%)
				H-3→L+1 (5.8%)
				H-3→L+10 (2.4%)
S_4	3.9890	310.81	0.3590	H-1→L (43.3%)
				H→L+2 (22.1%)
				H-3→L (20.7%)
				H-1→L+1 (2.5%)
				H-1→L+2 (2.5%)

Table S20 Emission wavelengths and oscillator strength calculated for BDIBD-ACE-keto[2nd].

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	1.7097	725.20	0.3215	H→L (98.5%)
S_2	2.3901	518.74	0.0107	H→L+1 (96.9%)
S_3	2.4428	507.55	0.0119	H→L+2 (97.4%)
S_4	3.4330	361.16	0.0009	H→L+3 (94.3%)
				H→L+5 (3.1%)

Table S21 Absorbance wavelengths and oscillator strength calculated for BDIBD-MeOH.

State	Energy (eV)	Absorption (nm)	oscillator strength	Transition configuration
S_1	3.6443	340.21	1.1679	H→L (82.9%)
				H→L+2 (5.4%)
				H→L+1 (2.4%)
S_2	4.2218	293.68	0.1189	H→L+1 (48.1%)
				H-2→L (22.8%)
				H-2→L+1 (8.9%)
				H→L+2 (6.7%)
				H→L (4.3%)
				H-1→L+2 (2.9%)
S_3	4.3008	288.28	0.2047	H-1→L (26.2%)
				H→L+2 (25.9%)
				H→L+1 (15.1%)
				H-1→L+1 (14.1%)
				H-1→L+2 (5.3%)
				H-2→L+2 (3.8%)
				H-2→L (3.2%)
				H→L (2.0%)
S_4	4.4948	275.84	0.6373	H→L+2 (31.2%)
				H-1→L (24.8%)
				H-2→L (14.1%)
				H-1→L+2 (12.9%)
				H-2→L+1 (4.9%)
				H→L+9 (2.7%)

Table S22 Emission wavelengths and oscillator strength calculated for BDIBD-MeOH-enol.

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	3.1774	390.21	1.2338	H→L (90.6%)
				H→L+2 (2.6%)
S_2	3.9712	312.21	0.1689	H→L+1 (42.6%)
				H-2→L (17.0%)
				H-1→L (12.6%)
				H→L+2 (10.1%)
				H-2→L+1 (8.7%)
				H→L (2.8%)
S_3	4.0342	307.33	0.2050	H-1→L (39.6%)
				H→L+1 (31.9%)
				H→L+2 (10.3%)
				H-2→L+1 (5.8%)
				H-1→L+1 (5.4%)
S_4	4.1961	295.48	0.5468	H→L+2 (53.6%)
				H-1→L (19.1%)
				H-1→L+2 (9.9%)
				H-2→L (5.5%)
				H-2→L+1 (4.8%)

Table S23 Emission wavelengths and oscillator strength calculated for BDIBD-MeOH-keto[1st].

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	2.4969	496.55	0.5047	H→L (63.3%)
				H→L+1 (30.9%)
				H→L+2 (4.0%)
S_2	3.0284	409.41	0.0344	H→L+1 (64.7%)
				H→L (32.9%)
S_3	3.6811	336.81	0.0245	H→L+2 (90.7%)
				H→L+1 (2.1%)
				H→L (2.0%)
S_4	3.9551	313.48	1.0498	H-1→L (58.7%)
				H-1→L+1 (28.8%)

Table S24 Emission wavelengths and oscillator strength calculated for BDIBD-MeOH-keto[2nd].

State	Energy (eV)	Emission (nm)	oscillator strength	Transition configuration
S_1	1.7766	697.89	0.3352	H→L (67.3%)
				H→L+2 (27.6%)
				H→L+1 (5.5%)
S_2	2.2689	546.45	0.0093	H→L+1 (38.9%)
				H→L+2 (31.2%)
				H→L (28.8%)
S_3	2.3559	526.27	0.0101	H→L+1 (54.7%)
				H→L+2 (40.4%)
				H→L (3.9%)
S_4	3.3327	372.02	0.0010	H→L+3 (98.5%)

Table S25 Calculated HOMO, LUMO energy of BDIBD-DMF.

	Energy (eV)			
	LUMO	LUMO+1	LUMO+2	LUMO+3
enol	-0.7563	-0.2032	0.1365	0.4630
keto[1st]	-0.5062	-0.3977	0.0153	0.4692
keto[2nd]	-0.5601	-0.5124	-0.2489	0.2774
	HOMO	HOMO-1	HOMO-2	HOMO-3
enol	-5.8423	-6.7445	-6.9207	-7.9517
keto[1st]	-4.9356	-6.3558	-7.0562	-7.2106
keto[2nd]	-3.8222	-6.4088	-6.6014	-6.7755

Table S26 Calculated HOMO, LUMO energy of BDIBD-ACE.

	Energy (eV)			
	LUMO	LUMO+1	LUMO+2	LUMO+3
enol	-0.9087	-0.1834	-0.0628	0.5923
keto[1st]	-0.7037	-0.5808	0.0354	0.2971
keto[2nd]	-0.6983	-0.4820	-0.4357	0.3812
	HOMO	HOMO-1	HOMO-2	HOMO-3
enol	-5.9434	-6.8778	-7.0072	-8.1234
keto[1st]	-5.1702	-6.4379	-7.2151	-7.5308
keto[2nd]	-4.1316	-6.5866	-6.9411	-7.0009

Table S27 Calculated HOMO, LUMO energy of BDIBD-MeOH.

	Energy (eV)			
	LUMO	LUMO+1	LUMO+2	LUMO+3
enol	-0.7782	-0.1994	-0.0219	0.5873
keto[1st]	-0.5400	-0.0273	0.2910	0.6806
keto[2nd]	-0.6096	-0.4708	-0.3975	0.3958
	HOMO	HOMO-1	HOMO-2	HOMO-3
enol	-5.7603	-6.7173	-6.8371	-8.1244
keto[1st]	-4.9382	-6.3347	-7.0592	-7.4584
keto[2nd]	-4.0268	-6.4386	-6.8091	-6.8925

Table S28 Calculated HOMO-LUMO gap of the crystals.

HOMO-LUMO gap / eV	BDIBD-DMF	BDIBD- ACE	BDIBD-MeOH
enol	5.0859	5.0347	4.9820
keto[1st]	4.4294	4.4665	4.3050
keto[2nd]	3.2621	3.4333	3.4172

Table S29 Calculated HOMO-LUMO+1 gap of the crystals.

HOMO-LUMO+1 gap / eV	BDIBD-DMF	BDIBD- ACE	BDIBD-MeOH
enol	5.6391	5.7600	5.5609
keto[1st]	4.5379	4.5894	4.9109
keto[2nd]	3.3098	3.6496	3.5560

**Table S30** Calculated bond lengths (Å) of BDIBD-DMF, BDIBD-ACE, BDIBD-MeOH on S_0 configuration.
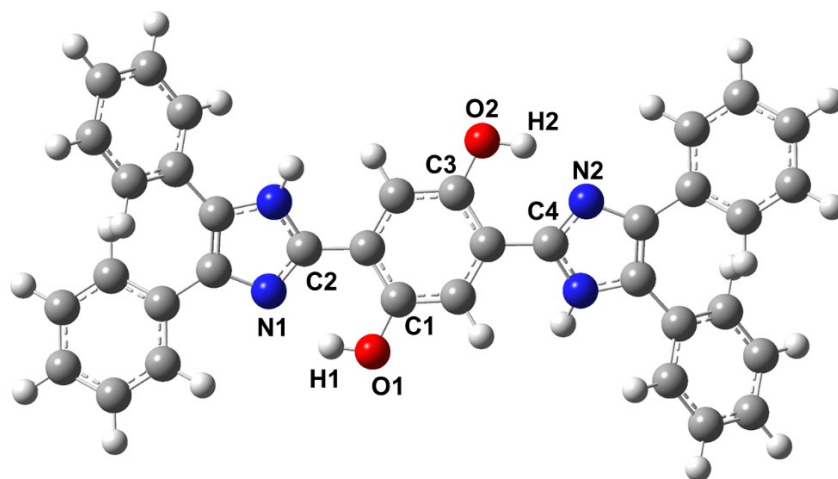
	BDIBD-DMF	**BDIBD-ACE**	**BDIBD-MeOH**
O1-H1	0.9757	0.9793	0.9854
O1-C1	1.354	1.351	1.356
N1-H1	1.972	1.857	1.775
N1-C2	1.324	1.323	1.323
O1-N1	2.833	2.730	2.664
O2-H2	0.9745	0.9790	0.9847
O2-C3	1.361	1.351	1.338
N2-H2	1.983	1.859	1.731
N2-C4	1.325	1.323	1.326
O2-N2	2.842	2.728	2.619

Table S31 Calculated Mayer bond order of BDIBD-DMF, BDIBD-ACE, BDIBD-MeOH on S_0 configuration.

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	0.97571	0.7693	0.7517
O1-C1	1.35425	0.9861	0.9737
N1-H1	1.97197	0.1138	0.1384
N1-C2	1.32447	1.3435	1.3206
O2-H2	0.97449	0.7706	0.7517
O2-C3	1.36148	0.9850	1.0385
N2-H2	1.98329	0.0506	0.1370
N2-C4	1.32462	1.3442	1.3093

**Table S32** Calculated bond lengths (Å) of BDIBD-DMF, BDIBD-ACE, BDIBD-MeOH on S_1 configuration.
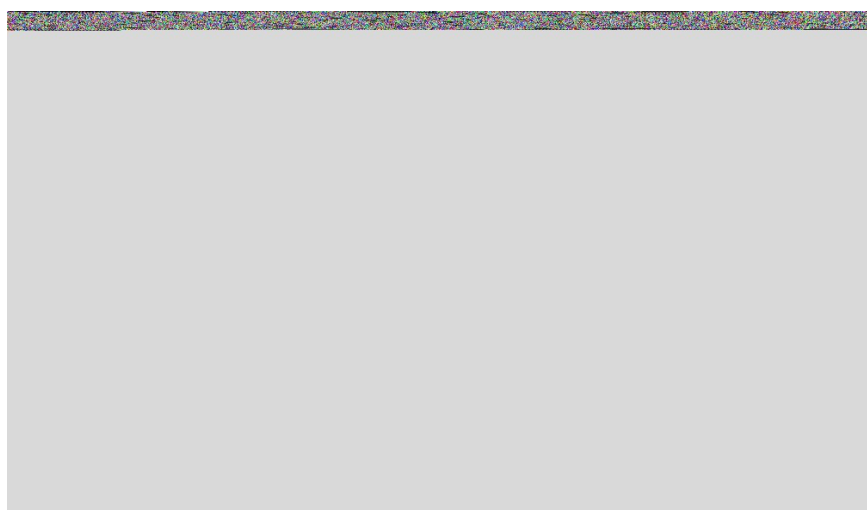
	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	0.9834	0.9917	1.003
O1-C1	1.339	1.334	1.335
N1-H1	1.878	1.760	1.679
N1-C2	1.350	1.348	1.346
O1-N1	2.763	2.660	2.601
O2-H2	0.9828	0.9916	1.002
O2-C3	1.340	1.335	1.321
N2-H2	1.878	1.759	1.653
N2-C4	1.350	1.348	1.350
O2-N2	2.764	2.660	2.571

Table S33 Calculated Mayer bond order of BDIBD-DMF, BDIBD-ACE, BDIBD-MeOH on S_1 configuration.

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	0.98340	0.7454	0.7224
O1-C1	1.33888	0.9993	0.9909
N1-H1	0.23046	0.1328	0.1601
N1-C2	1.34956	1.2946	1.2796
O2-H2	0.98278	0.7462	0.7231
O2-C3	1.33977	0.9983	1.0509
N2-H2	1.87838	0.1327	0.1560
N2-C4	1.35015	1.2957	1.2673

Table S34 Calculated bond lengths (Å) of BDIBD-DMF-keto[1st], BDIBD-ACE- keto[1st], BDIBD-MeOH-keto[1st] on S_1 configuration.
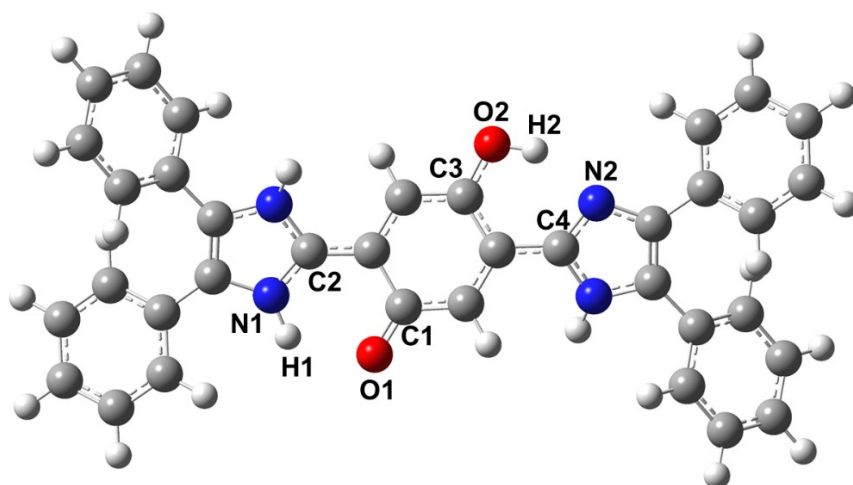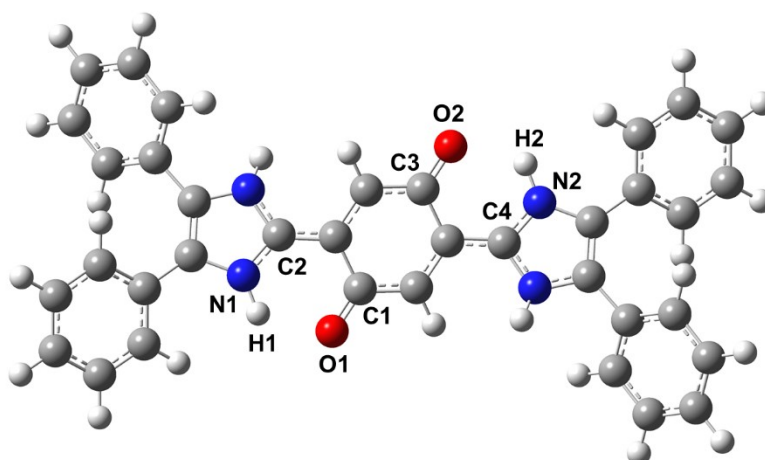

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	2.069	1.927	1.864
O1-C1	1.264	1.265	1.270
N1-H1	1.017	1.021	1.023
N1-C2	1.364	1.361	1.357
O1-N1	2.725	2.647	2.627
O2-H2	0.9847	0.9961	1.006
O2-C3	1.338	1.332	1.320
N2-H2	1.870	1.739	1.637
N2-C4	1.337	1.336	1.340
O2-N2	2.757	2.646	2.559

Table S35 Calculated Mayer bond order of BDIBD-DMF-keto[1st], BDIBD-ACE-keto[1st], BDIBD-MeOH-keto[1st] on S_1 configuration.

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	2.06859	0.1261	0.1417
O1-C1	1.26420	1.4342	1.3920
N1-H1	1.01687	0.7815	0.7710
N1-C2	1.36440	1.1395	1.1469
O2-H2	0.98470	0.7479	0.7256
O2-C3	1.33783	0.9773	1.0278
N2-H2	1.87039	0.1326	0.1540
N2-C4	1.33716	1.3111	1.2833

Table S36 Calculated bond lengths (Å) of BDIBD-DMF-keto[2nd], BDIBD-ACE-keto[2nd], BDIBD-MeOH-keto[2nd] on S1 configuration.

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	2.023	1.893	1.828
O1-C1	1.265	1.267	1.272
N1-H1	1.017	1.022	1.025
N1-C2	1.361	1.358	1.355
O1-N1	2.702	2.633	2.609
O2-H2	1.998	1.889	1.698
O2-C3	1.266	1.267	1.266
N2-H2	1.020	1.023	1.041
N2-C4	1.364	1.358	1.357
O2-N2	2.692	2.632	2.529

Table S37 Calculated Mayer bond order of BDIBD-DMF- keto[2nd], BDIBD-ACE-keto[2nd], BDIBD-MeOH-keto[2nd] on S_1 configuration.

	BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
O1-H1	2.02308	0.1457	0.1620
O1-C1	1.26517	1.3856	1.3445
N1-H1	1.01727	0.7679	0.7551
N1-C2	1.36128	1.0827	0.9858
O2-H2	1.99779	0.1461	0.1893
O2-C3	1.26620	1.3856	1.3630
N2-H2	1.01945	0.7663	0.7120
N2-C4	1.36390	1.1457	1.1509

Table S38 Calculated stretching vibration wavenumber (cm^{-1}) of O–H and N–H formed by proton transfer for BDIBD-DMF, BDIBD-ACE and BDIBD-MeOH in both S$_0$ and S$_1$ states.

		BDIBD-DMF	BDIBD-ACE	BDIBD-MeOH
S$_0$	O-H	3467	3370	3215
		3491	3379	3225
S$_1$-enol	O-H	3274	3081	2887
		3292	3098	2909
S$_1$-keto^{1st}-1	O-H	3267	3027	2861
	N-H	3377	3312	3260
S$_1$-keto^{1st} -2	O-H	3230	3022	2848
	N-H	3345	3304	3112
S$_1$-keto^{2nd}	O-H	3371	3279	3006
		3341	3288	3230

Table S39 Calculated density of all electrons ρ(BCP), potential energy density V(BCP) and hydrogen bond energy E_HB of hydrogen bond of BDIBD-DMF, BDIBD-ACE and BDIBD-MeOH in both S$_0$ and S$_1$ states.

		ρ(BCP) / a.u.	V(BCP) / a.u.	E_HB/ kcal mol^{-1}
BDIBD-DMF	Enol-S$_0$	0.0269	-0.0202	-5.27
		0.0262	-0.0197	-5.11
	Enol-S$_1$	0.0330	-0.0244	-6.63
		0.0330	-0.0244	-6.61
	Keto^{1st}-S$_1$	0.0337	-0.0336	-6.77
BDIBD- ACE	Enol-S$_0$	0.0350	-0.0265	-7.06
		0.0348	-0.0264	-7.03
	Enol-S$_1$	0.0441	-0.0336	-9.09
		0.0441	-0.0337	-9.11
	Keto^{1st}-S$_1$	0.0465	-0.0358	-9.63
BDIBD- MeOH	Enol-S$_0$	0.0426	-0.0328	-8.77
		0.0474	-0.0379	-9.83
	Enol-S$_1$	0.0541	-0.0434	-11.3
		0.0577	-0.0481	-12.1
	Keto^{1st}-S$_1$	0.0602	-0.0511	-12.7

*The relationship between hydrogen bond energy E_HB and potential energy density at corresponding BCP can be approximately described as:

$$E\_HB = -223.08 * \rho(BCP) + 0.7423$$