Supplementary Information

Tunable Optical Properties of Isoreticular UiO-67 MOFs for Photocatalysis: A Theoretical Study

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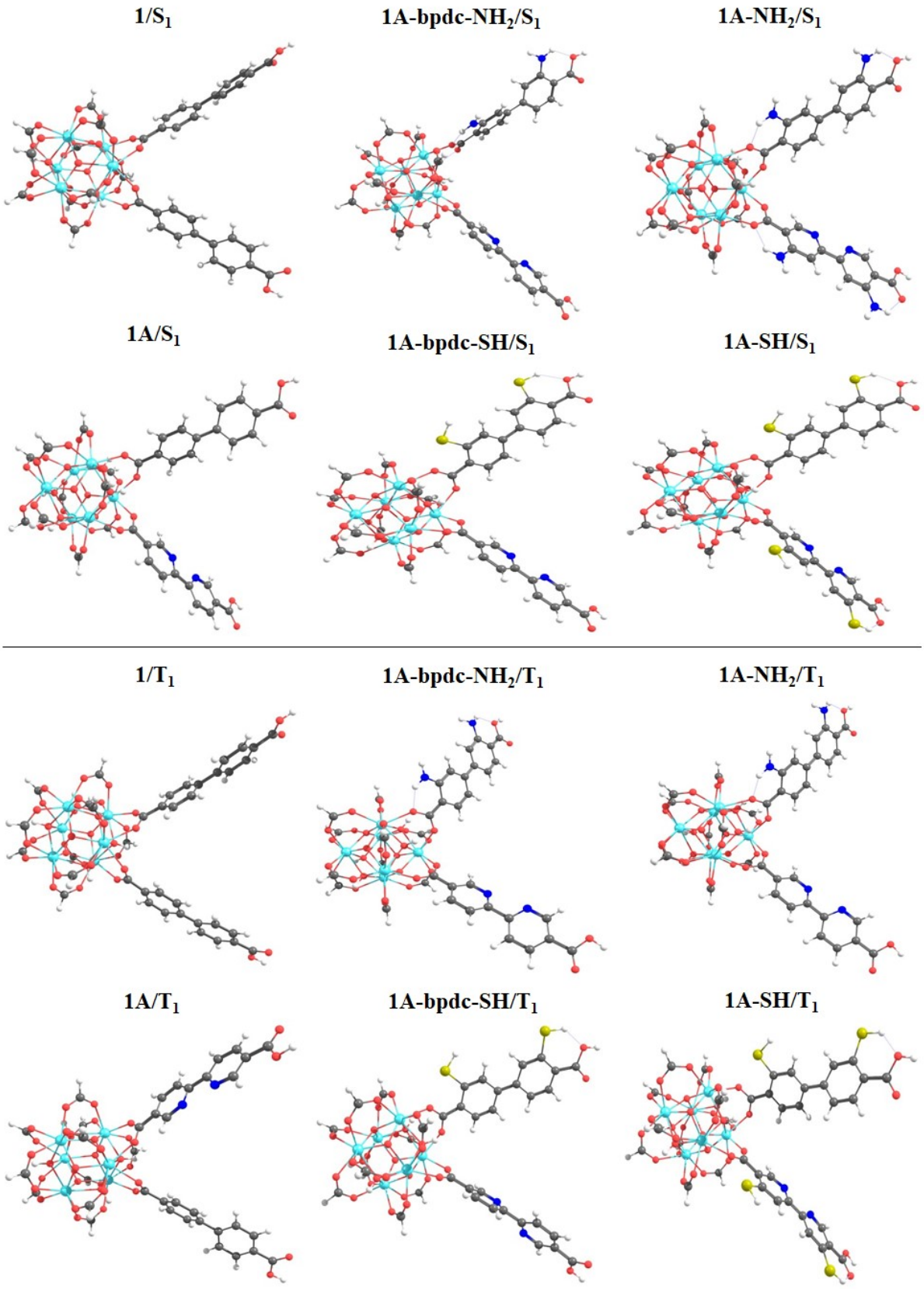


Figure S1. Optimized structures of the studied systems (**1**, **1A**, **1A**-bpdc-NH_2, **1A**-bpdc-SH, **1A**-NH_2 and **1A**-SH) in the S_1 and T_1 states via DFT/B3LYP/Def2-TZPP theory level. Atoms are denoted with light green (zirconium), gray (carbon), light gray (hydrogen), red (oxygen), darker blue (nitrogen), blue (zirconium) and yellow (sulfur) spheres.

***Table S1.** Structure parameters to the studied models (Node/linkers) in the S_0, S_1, and T_1 states via TDDFT/B3LYP/Def2-TZPP theory level. Where *d* is bond lengths, **δ** is the angle, and γ is torsion angles (in Å). *Nodo-$(bpdc)_2/S_0$ (**1**), Nodo-bpdc-bpydc/S_0 (**1A**). R1 and R2 is H, NH_2 and SH to **1A**, **1A**-NH_2 and **1A**-SH, respectively.

Parameters	1	1A	1A-NH_2	1A-SH	1	1A	1A-NH_2	1A-SH	1	1A	1A-NH_2	1A-SH
	S_0				S_1				T_1			
Nodo												
d(Zr1- Zr2)	3.564	3.567	3.568	3.566	3.562	3.563	3.532	3.540	3.565	3.561	3.506	3.563
d(Zr1- Zr3)	3.578	3.572	3.427	3.422	3.532	3.429	3.543	3.429	3.577	3.429	3.616	3.559
d(Zr2- Zr3)	3.424	3.426	3.573	3.574	3.502	3.569	3.704	3.587	3.424	3.567	3.373	3.434
d(Zr1- Zr4)	3.653	3.653	3.644	3.656	3.703	3.634	3.585	3.669	3.568	3.634	3.583	3.581
d(Zr2-O1)	2.191	2.209	2.194	2.199	2.175	2.206	2.261	2.123	2.190	2.222	2.129	2.196
d(Zr1-O2)	2.288	2.301	2.261	2.274	2.228	2.302	2.279	2.106	2.278	2.303	2.354	2.316
d(Zr4-O3)	2.332	2.321	2.351	2.368	2.262	2.300	2.231	2.448	2.320	2.293	2.168	2.291
δ(Zr1- Zr2- Zr3)	57.3	57.4	57.4	57.3	59.2	57.5	56.8	57.5	57.3	57.5	56.5	57.6
δ(Zr3- Zr1- Zr4)	90.1	90.0	89.8	90.0	90.4	90.0	88.1	89.1	89.0	89.9	89.6	89.9
δ(Zr1- O4- Zr2)	117.3	117.4	117.5	117.5	118.3	116.8	116.2	116.6	117.3	116.9	116.9	116.7
δ(Zr1- O4- Zr3)	109.2	109.1	109.1	109.0	110.2	109.2	110.6	110.1	107.1	109.2	109.6	108.7
γ(Zr1-O1-O2- Zr2)	4.7	4.5	3.9	3.7	4.4	2.1	1.8	1.2	4.8	0.9	-11.0	1.5
γ(Zr4-O3-O5- Zr5)	0.3	1.1	-0.4	0.1	-0.6	-0.4	-0.5	-1.2	0.2	-0.5	-0.8	1.9
bpdc												
d(C-R1)	1.081	1.081	1.369	1.771	1.090	1.088	1.241	1.760	1.081	1.087	1.371	1.770
d(C-R2)	1.080	1.080	1.364	1.771	1.089	1.088	1.362	1.739	1.081	1.088	1.368	1.771
γ(OH-C1-C2-C3)	0.3	-1.7	3.7	13.9	0.1	-0.2	1.8	2.1	0.7	-0.2	-2.6	5.4
γ(C4-C5-C6-C7)	**-38.7**	**-38.2**	**-37.3**	**-39.5**	**-16.3**	**-35.4**	**-40.1**	**-38.2**	**-0.6**	**-35.5**	**-38.5**	**-36.6**
γ(C8-C9-C10-O)	179.6	-178.1	-177.7	169.3	-179.9	179.6	-179.7	177.5	-179.4	179.6	-175.8	176.4
γ(C1-C2-C-R1)	3.5	-0.1	3.7	2.6	0.6	0.7	-1.5	0.9	-0.3	0.7	-3.5	2.4
γ(C10-C9-C-R2)	0.4	4.8	-7.0	-4.2	1.1	0.2	2.1	0.8	3.5	0.2	3.5	-9.2
bpydc												
d(N-N)	-	2.833	2.855	2.847	-	2.452	1.373	2.737	-	2.452	2.691	2.694
d(C-R1)	-	1.081	1.362	1.770	-	1.088	1.362	1.759	-	1.088	1.351	1.757
d(C-R2)	-	1.080	1.373	1.758	-	1.089	1.739	1.770	-	1.088	1.354	1.767
γ(OH-C1-C2-C3)	-	-1.4	-1.4	-2.2	-	-0.1	0.7	0.2	-	-0.1	-0.8	-0.8
γ(N1-C4-C5-N2)	-	**-37.7**	**-39.8**	**-38.7**	**-**	**-0.1**	**14.5**	**5.9**	**-**	**-0.1**	**-0.1**	**0.6**
γ(C6-C7-C8-O1)	-	175.6	171.7	173.6	-	179.2	178.9	179.6	-	179.2	177.7	-178.9
γ(C1-C2-C-R1)	-	1.2	2.6	1.4	-	0.0	2.7	-0.4	-	0.0	1.3	0.1
γ(C10-C9-C-R2)	-	-0.5	-6.6	-0.4	-	-0.6	-6.6	-1.6	-	-0.1	-2.9	0.0

Table S2. Most intense singlet→singlet absorption transitions and $S_1 \rightarrow S_0$ deactivation data to the studied systems via TDDFT/B3LYP/ Def2-TZPP theory level. Where λ_a and λ_e is the theoretical absorption and emission wavelength in nm, respectively (& experimental values); *f* is the oscillator strength, H (HOMO), and L (LUMO); A is assignment transitions; k_{rad} and τ_{rad} are the radiative transition rate (in s^{-1}) and lifetime (in seconds).

Systems	Absorption (S_0)				Deactivation (S_1)				
	λ_a	*f*	Active MOs	A ($S_0 \rightarrow S_n$)	λ_e	*f*	k_{rad}	τ_{rad}	A ($S_1 \rightarrow S_0$)
1	295 (365)&	0.394	H→L	π→ π* (bpdc)	339 398&	1.278	$1.8*10^9$	$5.3*10^{-10}$	π*→ π (bpdc)
	292	0.302	H-1→L	π→ π* (bpdc)					
	283	1.563	H→L+1	π→ π* (bpdc)					
1A	290	0.923	H→L+1	π→ π* (bpdc)	605 467&	$0.4*10^{-5}$	$0.2*10^6$	$4.3*10^{-6}$	π*→ n (bpydc)
	282	0.783	H-1→L	π→ π* (bpydc)					
	280	0.695	H-3→L	n→ π* (bpydc)	318 398&	1.171	$0.2*10^{10}$	$5.1*10^{-10}$	π*→ π (bpdc)
1A-(bpdc-NH_2)	357	0.208	H→L+1	n→ π* (bpdc-NH_2)	404	0.039	$1.0*10^5$	$9.8*10^{-6}$	π*→ n (bpydc)
	281	0.569	H-3→L	π→ π* (bpydc)					
	276	0.467	H-6→L	n→ π* (bpydc)	386	0.707	$0.1*10^{10}$	$9.0*10^{-10}$	π*→ π (bpdc-NH_2)
1A-(bpdc-SH)	358	0.044	H→L+1	n → π* (bpdc-SH)	439	$0.5*10^{-4}$	$4.1*10^4$	$2.4*10^{-5}$	π*→ n (bpydc)
	287	0.334	H-1→L+1	n→ π* (bpdc-SH)					
	283	0.371	H-2→L+1	π → π* (bpdc-SH)	378	0.059	$7.0*10^7$	$1.4*10^{-8}$	π*→ π (bpdc-SH)
	281	0.355	H-3→L	π→ π* (bpydc)					
1A-(NH_2)	362	0.135	H→L	n→ π* (bpdc-NH_2)	414	0.002	$2.6*10^6$	$3.8*10^{-8}$	π*→ n (bpydc)
	290	0.186	H-4→L	π → π* (bpdc-NH_2)					
	275	0.531	H-2→L+6	n→ π* (bpydc-NH_2)	392	0.024	$2.6*10^7$	$3.9*10^{-8}$	π*→ π (bpdc-NH_2)
1A-(SH)	378	0.061	H→L+3	n → π* (bpdc-SH)	404	0.040	$0.1*10^9$	$8.4*10^{-9}$	π*→ n (bpydc-SH)
	348	0.140	H-9→L	π→ π* (bpydc-SH)					
	283	0.350	H→L+10	n→ π* (bpdc-SH→O)	396	0.070	$7.5*10^7$	$1.3*10^{-8}$	π*→ π (bpdc-SH)

Table S3. Most intense singlet→singlet absorption transitions and $S_1 \rightarrow S_0$ deactivation data to the studied systems via TDDFT/CAM-B3LYP/ Def2-TZPP theory level.

	Absorption (S_0)				Deactivation (S_1)				
Systems	λ_a	f	**Active MOs**	**A**	λ_e	f	$k_{rad}*10^{10}$	$\tau_{rad}*10^{-10}$	**A**
1	264	0.881	H→L	π→ π*	313	1.660	$0.3*10^{10}$	$3.5*10^{-10}$	π*→ π (bpdc)
	259	2.016	H→L+1	π→ π*					
	208	0.010	H-3→L	π→ π*					
1A	264	0.893	H→L+1	π→ π* (bpdc)	480	0.010	$0.3*10^{5}$	$3.1*10^{-5}$	π*→ n (bpydc)
	257	1.747	H-1→L	π→ π* (bpydc)					
	229	0.259	H-3→L	n→ π* (bpydc)	297	1.550	$0.3*10^{10}$	$3.4*10^{-10}$	π*→ π (bpdc)
1A-(bpdc-NH_2)	299	0.133	H→L+1	n→ π* (bpdc)	413	0.003	$1.6*10^{5}$	$5.1*10^{-6}$	π*→ n (bpydc)
	259	0.421	H-2→L+1	π→ π* (bpydc)					
	255	1.533	H-3→L	n→ π* (bpydc)	240	0.004	$0.57*10^{10}$	$1.7*10^{-10}$	π*→ π (bpdc-NH_2)
1A-(bpdc-SH)	297	0.139	H→L+5	π → π* (bpdc)	362	0.004	$4.9*10^{6}$	$2.5*10^{-7}$	π*→ n (bpydc)
	260	0.504	H-2→L+1	π→ π* (bpydc)					
	256	1.668	H-2→L+5	n→ π* (bpdc)	308	1.392	$0.25*10^{10}$	4.0	π*→ π (bpdc-SH)
1A-(NH_2)	324	0.259	H→L+5	π → π* (bpdc)	319	0.054	$8.8*10^{6}$	$1.2*10^{-7}$	π*→ n (bpydc)
	293	1.589	H-7→L	π → π* (bpydc)					
	251	0.362	H-9→L	π→ π* (bpdc)	324	0.260	$3.9*10^{7}$	$2.5*10^{-8}$	π*→ π (bpdc-NH_2)
	244	0.243	H-2→L+6	n→ π* (bpydc)					
1A-(SH)	317	0.163	H-4→L	n → π* (bpdc)	330	0.104	$0.2*10^{9}$	$6.2*10^{-9}$	π*→ n (bpydc-SH)
	306	0.262	H→L+2	n→ π* (bpdc)					
	299	1.352	H-5→L	n → π* (bpydc)	306	0.206	$0.5*10^{9}$	$2.1*10^{-9}$	π*→ π (bpdc-SH)

*Where λ_a is the theoretical absorption wavelength in nm (& experimental emission wavelength), f is the oscillator strength, H (HOMO), and L (LUMO). Methanol Solutions, Ɛ=32.63 and refraction=1.329. &Experimental absorption wavelength.

*__Table S4.__ $T_1 \rightarrow S_0$ deactivation data to the systems via TDDFT/CAM-B3LYP and B3LYP/ Def2-TZPP theory level.

B3LYP	λ_e	*f*	Assignment
1	346	1.089	π*→ π (bpdc)
1A	572	$2.1*10^{-6}$	π*→ π (bpydc)
	317	0.926	π*→ π (bpdc)
1A-(bpdc-NH_2)	419	0.290	π*→ π (bpdc)
	336	0.0001	π*→ π (bpydc)
1A-(bpdc-SH)	411	0.114	π*→ π (bpdc)
	332	0.081	π*→ π (bpydc)
1A-(NH_2)	419	0.258	π*→ π (bpdc)
	327	0.063	π*→ π (bpydc)
1A-(SH)	388	0.018	π*→ π (bpdc)
	303	0.007	π*→ π (bpydc)
CAM-B3LYP			
1	329	1.631	π*→ π (bpdc)
1A	461	$1.2*10^{-6}$	π*→ π (bpydc)
	298	1.548	π*→ π (bpdc)
1A-(bpdc-NH_2)	365	0.452	π*→ π (bpdc)
	290	0.001	π*→ π (bpydc)
1A-(bpdc-SH)	347	0.364	π*→ π (bpdc)
	307	1.094	π*→ π (bpydc)
1A-(NH_2)	434	0.001	π*→ π (bpdc)
	288	0.002	π*→ π (bpydc)
1A-(SH)	321	0.593	π*→ π (bpdc)
	308	0.599	π*→ π (bpydc)

*Where λ_e is the theoretical emission wavelength in nm (& experimental emission wavelength), *f* is the oscillator strength, k_{rad} and τ_{rad} are the radiative transition rate (in s^{-1}) and lifetime (in seconds).

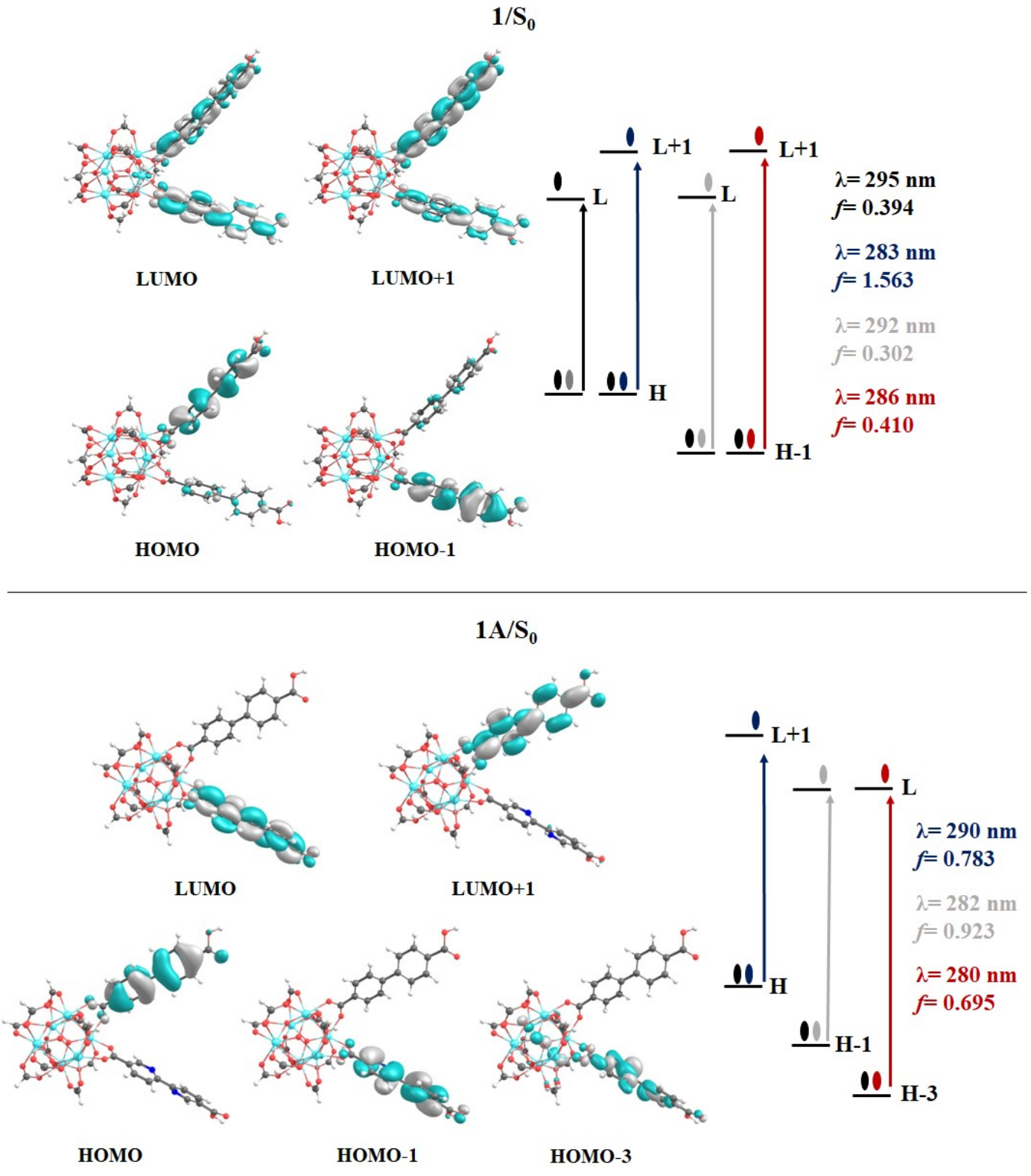


Figure S2. Frontier Molecular Orbitals (FMOs) are involved in the most intense singlet→singlet absorption transitions to the studied systems **1** and **1A** via TDDFT/B3LYP/Def2-TZPP theory level. Atoms are denoted with gray (carbon), light gray (hydrogen), red (oxygen), darker blue (nitrogen), and blue (zirconium) spheres. Isosurface contour values are set as 0.03.

***Table S5.** Structure parameters to the **bpdc**, **bpydc**, and proposed substituents (with -NH_2 and -SH) in the S_0, S_1, and T_1 states via TDDFT/B3LYP/Def2-TZPP theory level. Where *d* is bond lengths and γ is torsion angles (in Å).

Parameters	**bpdc/S_0**	**bpdc-NH_2 /S_0**	**bpdc-SH /S_0**	**bpydc/S_0**	**bpydc-NH_2 /S_0**	**bpydc-SH /S_0**
d(N-N)	-	-	-	2.676	2.846	2.814
d(C-R1)	1.081	1.361	1.769	1.081	1.350	1.760
d(C-R2)	1.081	1.369	1.770	1.081	1.356	1.761
γ(HO -C1-C2-C3)	3.9	-1.9	0.9	3.9	-2.0	0.6
γ(C4-C5-C6-C7)	-1.7	**-40.0**	**-38.8**	-	-	-
γ(N2-C4-C7-N2)	-	-	-	**-1.7**	**-44.2**	**-38.6**
γ(C8-C9-C10-OH)	177.2	-176.4	-172.3	-177.2	-178.3	-170.6
γ(C1-C2-C-R1)	2.6	-2.4	0.4	0.0	-0.6	0.3
γ(C10-C9-C-R2)	-3.0	3.8	2.1	-0.1	2.2	1.3
	bpdc/S_1	**bpdc-NH_2 /S_1**	**bpdc-SH /S_1**	**bpydc/S_1**	**bpydc-NH_2 /S_1**	**bpydc-SH /S_1**
d(N-N)	-	-	-	2.408	2.374	2.403
d(C-R1)	1.081	1.351	1.757	1.081	1.350	1.761
d(C-R2)	1.081	1.376	1.775	1.081	1.355	1.762
γ(HO-C1-C2-C3)	0.2	-0.3	0.5	-0.1	0.4	0.3
γ(C4-C5-C6-C7)	-1.1	-9.6	-8.0	-	-	-
γ(N2-C4-C7-N2)	-	-	-	-1.7	0.2	0.1
γ(C6-C7-C8-OH)	179.8	177.3	180.0	179.8	-179.4	179.8
γ(C1-C2-C3-R1)	-0.4	0.1	1.2	2.6	0.1	0.1
γ(R2-C9-C7-C8)	-0.8	4.3	0.7	-3.6	0.7	0.0
	bpdc/T_1	**bpdc-NH_2 /T_1**	**bpdc-SH /T_1**	**bpydc/T_1**	**bpydc-NH_2 /T_1**	**bpydc-SH /T_1**
d(N-N)	-	-	-	2.367	2.344	2.362
d(C-R1)	1.081	1.348	1.764	1.081	1.352	1.762
d(C-R2)	1.080	1.365	1.760	1.080	1.358	1.764
γ(HO -C1-C2-C3)	1.0	-1.0	-1.3	0.0	0.7	0.6
γ(C4-C5-C6-C7)	-0.2	-4.6	-4.3	-	-	-
γ(N2-C4-C7-N2)	-	-	-	0.3	0.4	0.1
γ(C6-C7-C8-OH)	-179.5	-179.2	-174.1	-178.5	-178.9	177.5
γ(C1-C2-C3-R1)	-0.2	0.7	0.5	-0.2	0.5	0.2
γ(R2-C9-C7-C8)	-0.4	3.2	9.3	-0.3	0.8	-0.7

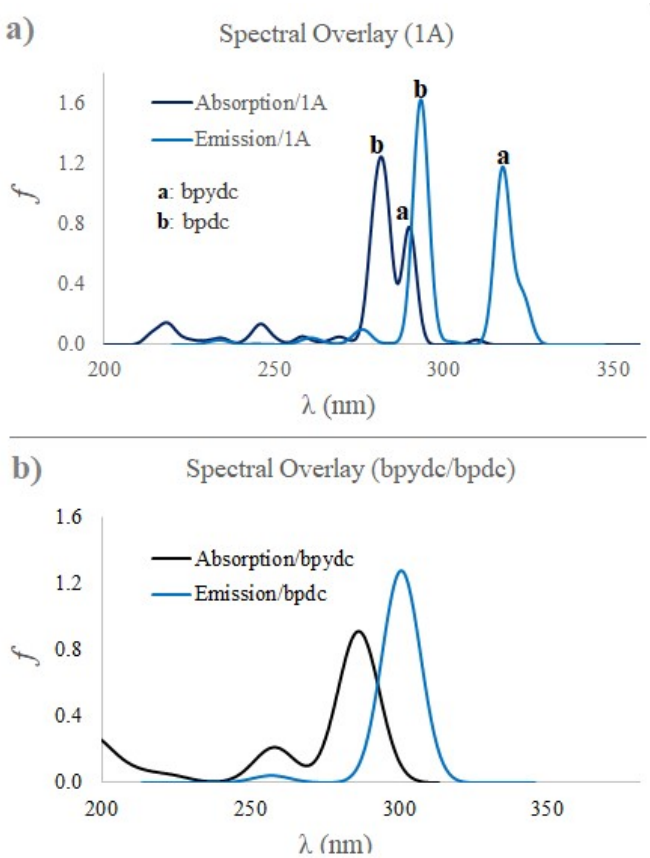


Figure S3. Computed spectral overlap to **a) 1A** and **b)** free ligands.

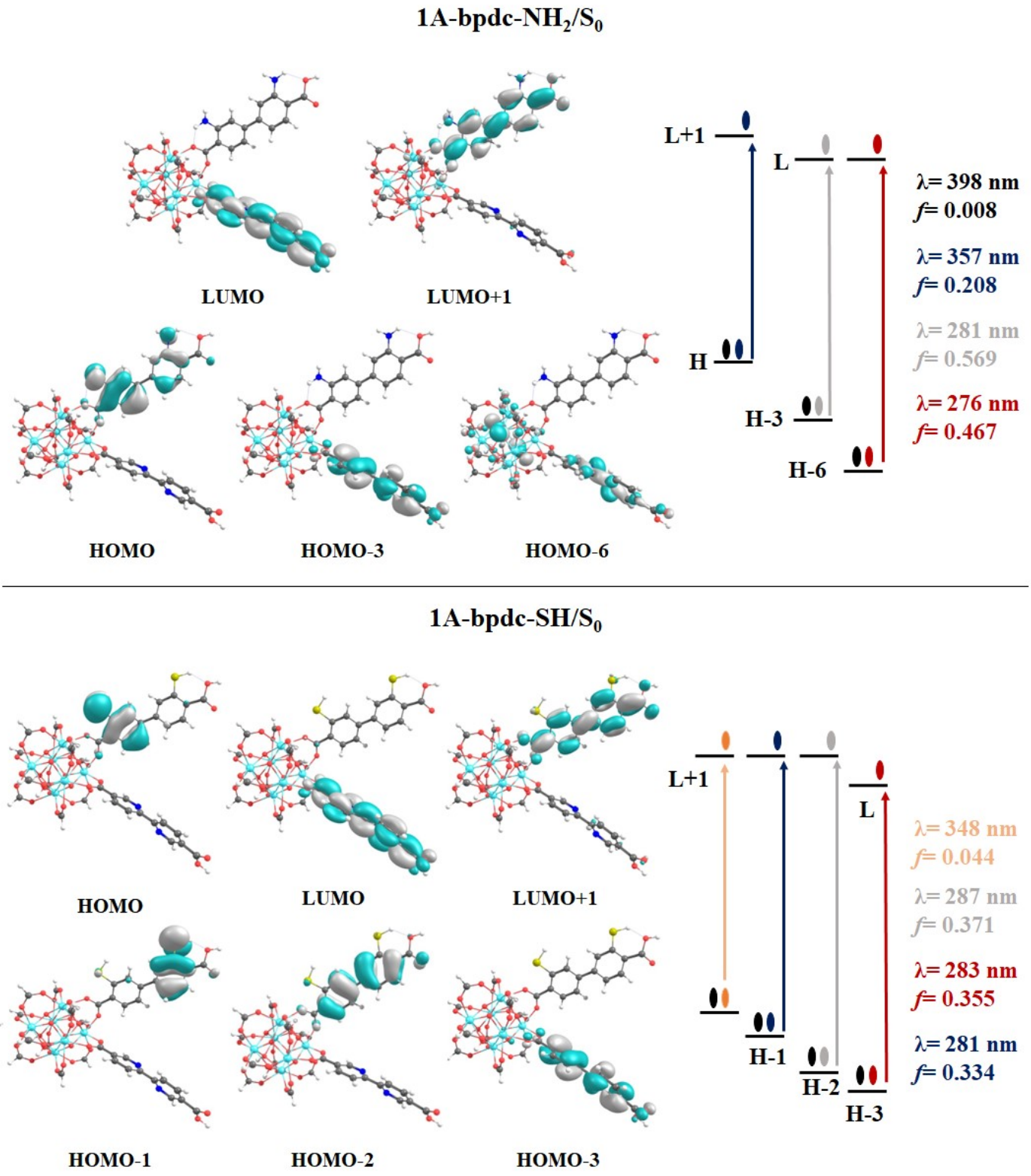


Figure S4. Schematic representation of the Frontier Molecular Orbitals (FMOs) involved in the most intense singlet→singlet absorption transitions to the proposed systems **1A-bpdc-NH$_2$** and **1A-bpdc-SH** via TDDFT/B3LYP/Def2-TZPP theory level. Atoms are denoted with gray (carbon), light gray (hydrogen), red (oxygen), darker blue (nitrogen), and blue (zirconium), and yellow (sulfur) spheres. Isosurface contour values are set as 0.03.

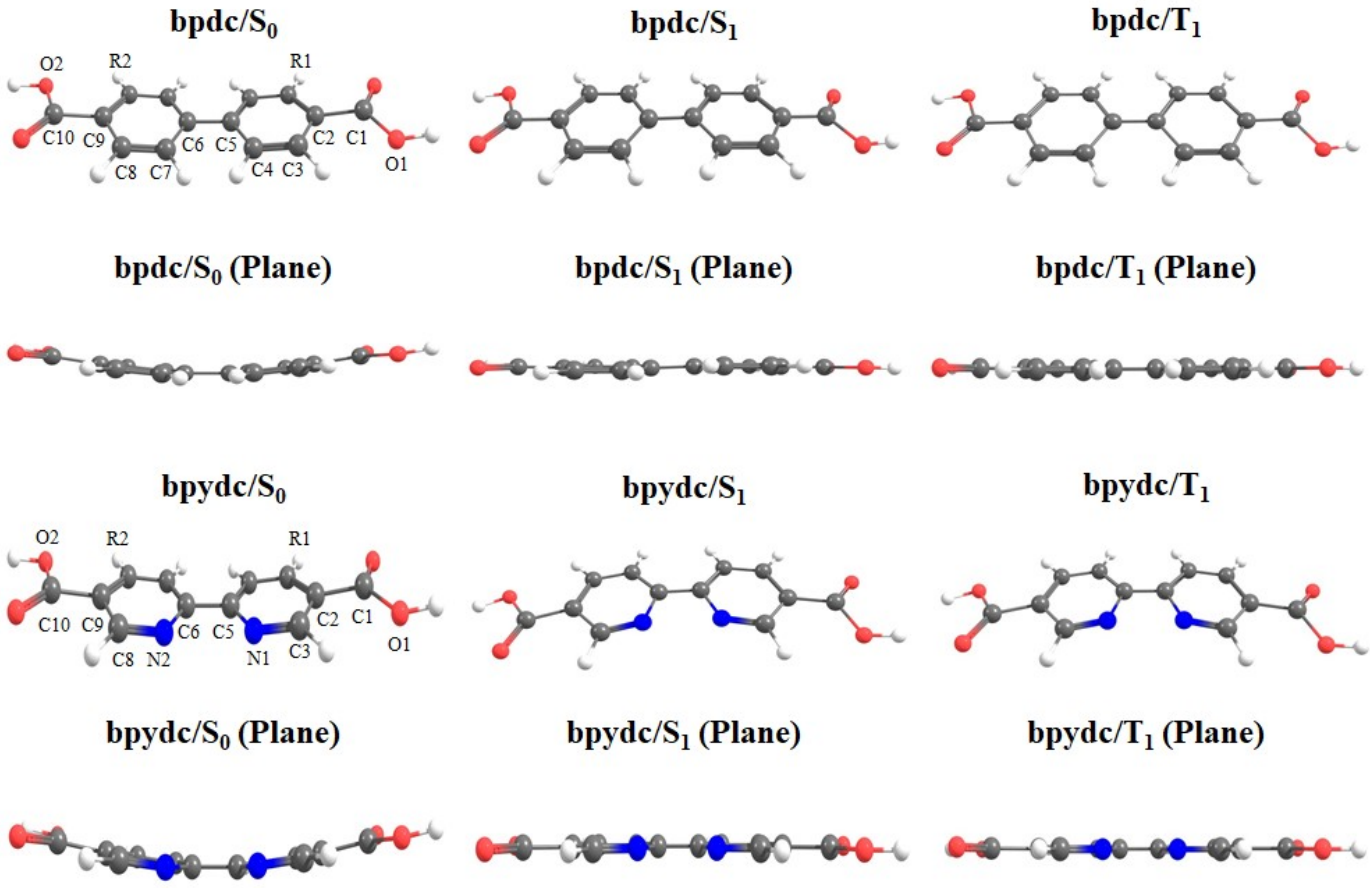


Figure S5. Optimized structures of the free linkers bpdc and bpydc in two perspectives to the S_1 and T_1 states via DFT/B3LYP/Def2-TZPP theory level. Atoms are denoted with gray (carbon), light gray (hydrogen), red (oxygen), blue (nitrogen), and yellow (sulfur) spheres.

***Table S6.** Structure parameters to the **bpdc**, **bpydc**, and proposed ligands (with -NH_2 and -SH) in the S_0, S_1, and T_1 states via TDDFT/B3LYP/Def2-TZPP theory level. Where *d* is bond lengths and γ is torsion angles (in Å).

Parameters	**bpdc/S_0**	**bpdc-NH_2 /S_0**	**bpdc-SH /S_0**	**bpydc/S_0**	**bpydc-NH_2 /S_0**	**bpydc-SH /S_0**
d(N-N)	-	-	-	2.676	2.846	2.814
d(C-R1)	1.081	1.361	1.769	1.081	1.350	1.760
d(C-R2)	1.081	1.369	1.770	1.081	1.356	1.761
γ(HO -C1-C2-C3)	3.9	-1.9	0.9	3.9	-2.0	0.6
γ(C4-C5-C6-C7)	-1.7	**-40.0**	**-38.8**	-	-	-
γ(N2-C4-C7-N2)	-	-	-	**-1.7**	**-44.2**	**-38.6**
γ(C8-C9-C10-OH)	177.2	-176.4	-172.3	-177.2	-178.3	-170.6
γ(C1-C2-C-R1)	2.6	-2.4	0.4	0.0	-0.6	0.3
γ(C10-C9-C-R2)	-3.0	3.8	2.1	-0.1	2.2	1.3
	bpdc/S_1	**bpdc-NH_2 /S_1**	**bpdc-SH /S_1**	**bpydc/S_1**	**bpydc-NH_2 /S_1**	**bpydc-SH /S_1**
d(N-N)	-	-	-	2.408	2.374	2.403
d(C-R1)	1.081	1.351	1.757	1.081	1.350	1.761
d(C-R2)	1.081	1.376	1.775	1.081	1.355	1.762
γ(HO-C1-C2-C3)	0.2	-0.3	0.5	-0.1	0.4	0.3
γ(C4-C5-C6-C7)	-1.1	-9.6	-8.0	-	-	-
γ(N2-C4-C7-N2)	-	-	-	-1.7	0.2	0.1
γ(C6-C7-C8-OH)	179.8	177.3	180.0	179.8	-179.4	179.8
γ(C1-C2-C3-R1)	-0.4	0.1	1.2	2.6	0.1	0.1
γ(R2-C9-C7-C8)	-0.8	4.3	0.7	-3.6	0.7	0.0
	bpdc/T_1	**bpdc-NH_2 /T_1**	**bpdc-SH /T_1**	**bpydc/T_1**	**bpydc-NH_2 /T_1**	**bpydc-SH /T_1**
d(N-N)	-	-	-	2.367	2.344	2.362
d(C-R1)	1.081	1.348	1.764	1.081	1.352	1.762
d(C-R2)	1.080	1.365	1.760	1.080	1.358	1.764
γ(HO -C1-C2-C3)	1.0	-1.0	-1.3	0.0	0.7	0.6
γ(C4-C5-C6-C7)	-0.2	-4.6	-4.3	-	-	-
γ(N2-C4-C7-N2)	-	-	-	0.3	0.4	0.1
γ(C6-C7-C8-OH)	-179.5	-179.2	-174.1	-178.5	-178.9	177.5
γ(C1-C2-C3-R1)	-0.2	0.7	0.5	-0.2	0.5	0.2
γ(R2-C9-C7-C8)	-0.4	3.2	9.3	-0.3	0.8	-0.7

*Experimental reported data to MIL125-NH_2 system obtained via powder diffraction[66].

Table S7. Most intense singlet→singlet absorption transitions data to **bpdc**, **bpydc**, and proposed substituents (with -NH_2 and -SH) via TDDFT theory level.

	B3LYP			CAM-B3LYP			
Systems	λ_a	*f*	**Active MOs**	λ_a	*f*	**Active MOs**	**A**
bpdc	288	1.043	H→L	267	1.059	H→L	π→ π*
	203	0.291	H-1→L+1	180	1.030	H-1→L+1	π→ π*
bpdc-NH_2	347	0.128	H→L	304	0.237	H→L	π→ π*
	271	0.773	H-2→L	297	0.131	H-1→L	π→ π*
	220	0.266	H-1→L+3	251	0.634	H-2→L	π→ π*
	201	0.334	H-6→L	209	0.773	H→L+2	π→ π*
bpdc-SH	347	0.045	H→L	294	0.079	H→L	π→ π*
	340	0.061	H-1→L	291	0.117	H-1→L	π→ π*
	281	0.431	H-2→L	255	0.754	H-2→L	π→ π*
	240	0.450	H-1→L+3	225	0.773	H→L+2	π→ π*
	212	0.108	H-2→L+3	192	0.204	H-2→L+3	π→ π*
bpydc	385	0.002	H→L	328	0.004	H→L	π→ π*
	287	0.727	H-1→L	268	0.920	H-1→L	π→ π*
	258	0.200	H-1→L+1	239	0.186	H-1→L+1	π→ π*
bpydc-NH_2	323	0.046	H→L	281	0.065	H→L	π→ π*
	267	0.401	H-3→L	276	0.034	H-1→L	π→ π*
	209	0.177	H-3→L+2	240	0.867	H-2→L	π→ π*
	195	0.238	H→L+3	198	0.734	H-1→L+2	π→ π*
bpydc-SH	334	0.042	H→L	288	0.042	H→L	π→ π*
	274	0.691	H-3→L	272	0.113	H-1→L	π→ π*
	236	0.316	H-1→L+3	249	0.767	H-2→L	π→ π*
	197	0.233	H-6→L+1	220	0.850	H-1→L+2	π→ π*

*__Table S8.__ $S_1 \rightarrow S_0$ emission data to the systems via TDDFT theory level

	B3LYP		CAM-B3LYP		
Linkers	λ_e	*f*	λ_e	*f*	**Assignment**
bpdc	317	1.350	301	1.276	π*→ π
bpdc- NH_2	404	0.115	348	0.207	π*→ π
bpdc-SH	402	0.030	332	0.067	π*→ π
bpydc	600	$0.1*10^{-2}$	480	$0.4*10^{-5}$	π*→ π
bpydc- NH_2	621	$0.1*10^{-4}$	494	$0.2*10^{-5}$	π*→ π
bpydc-SH	603	$0.2*10^{-5}$	480	$0.4*10^{-6}$	π*→ π

*Where λ_e is the theoretical emission wavelength in nm (experimental emission wavelength is XXX nm), *f* is the oscillator strength, k_{rad} and τ_{rad} are the radiative transition rate (in s^{-1}) and lifetime (in seconds).

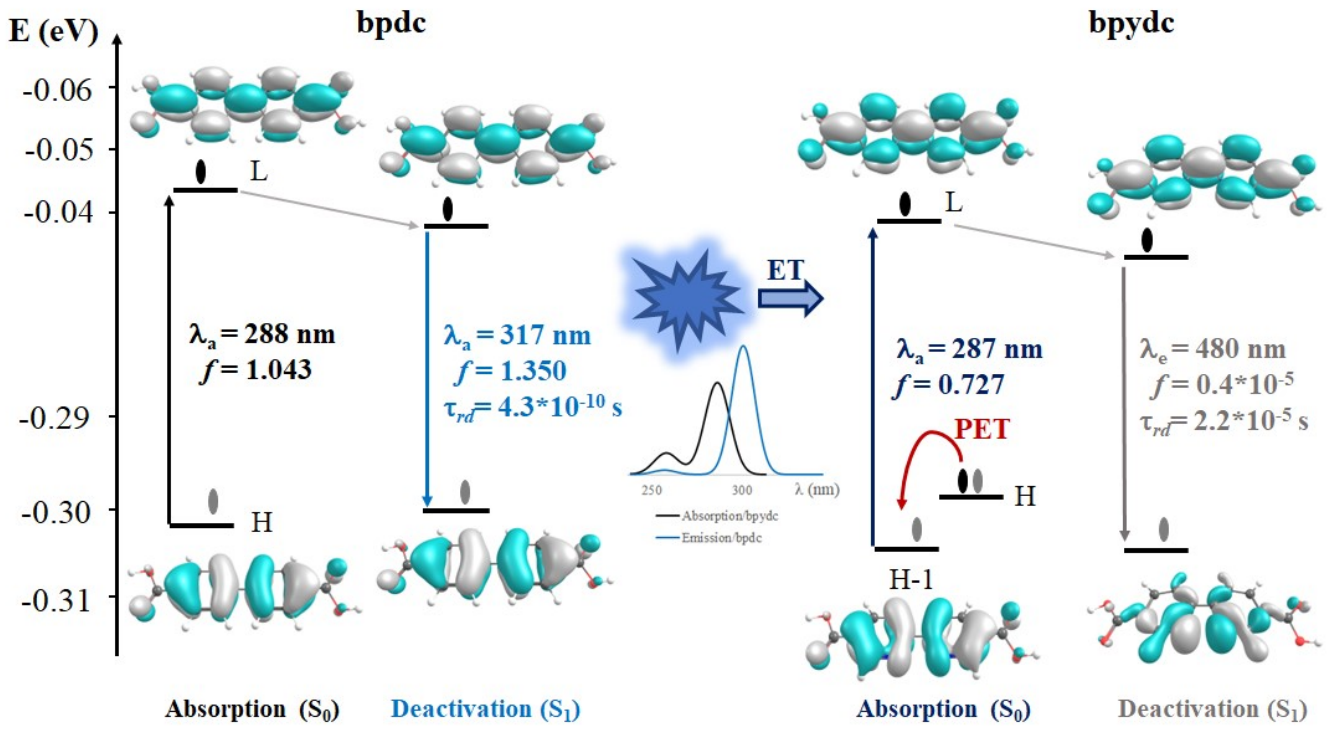


Figure S6. Schematic representation of the photophysical mechanism based on FMOs analysis on the S_0 (absorption) and S_1 states to free bpdc and bpydc linkers. Where, λ_a and λ_e are the computed wavelength of absorption (black and dark blue) and deactivation (light blue and gray), respectively; *f* is the oscillator strength; τ_{rad} is the radiative transition lifetime and ET is energy transfer. The spectral overlap (emission bpdc/absorption at bpydc) is represented. Isosurface contour values are set as 0.03 with TDDFT/Def2-TZPP/ B3LYP theory level.

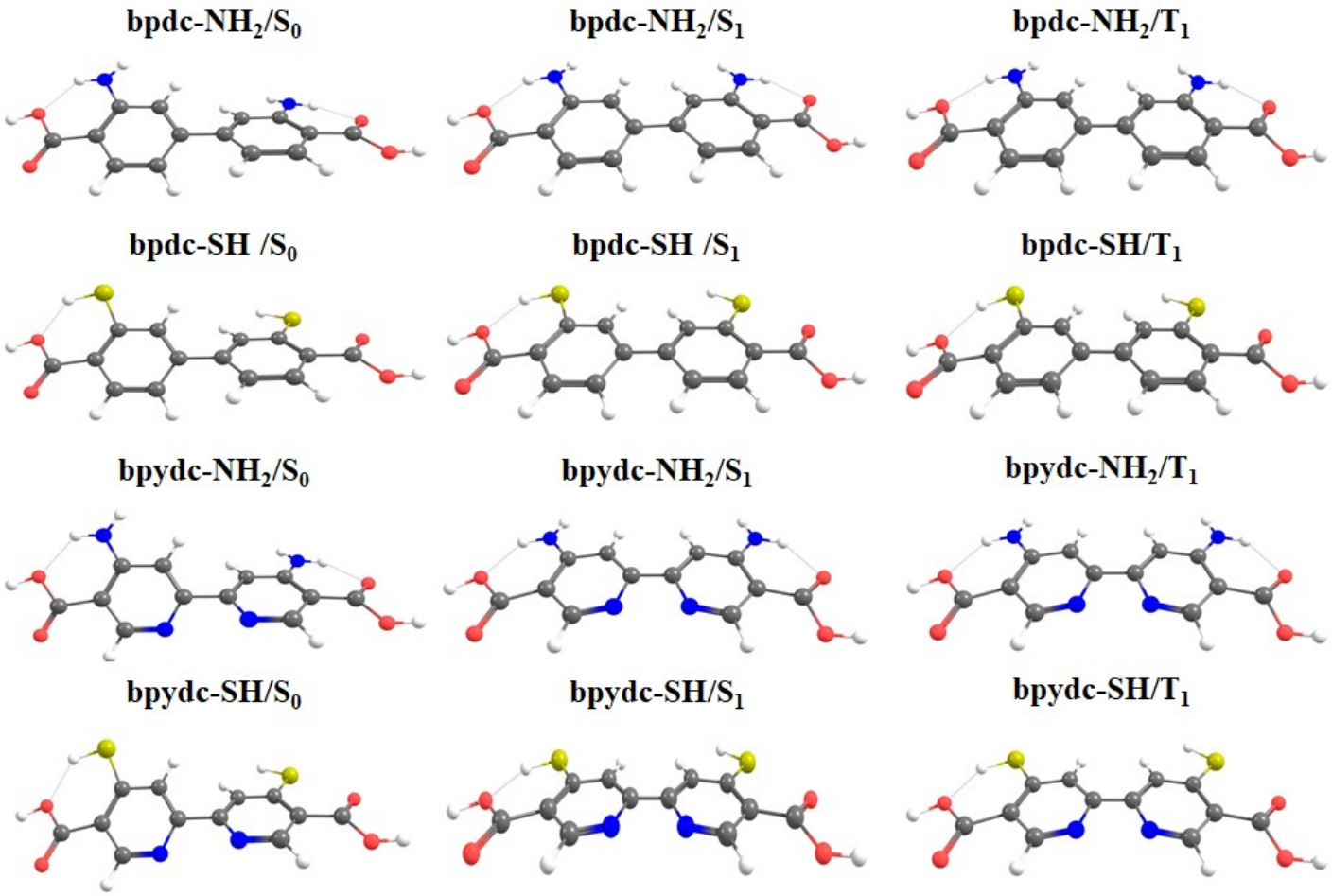


Figure S7. Optimized structures of the free linkers bpdc and bpydc in two perspectives to the S_1 and T_1 states via DFT/B3LYP/Def2-TZPP theory level. Atoms are denoted with gray (carbon), light gray (hydrogen), red (oxygen), blue (nitrogen), and yellow (sulfur) spheres.

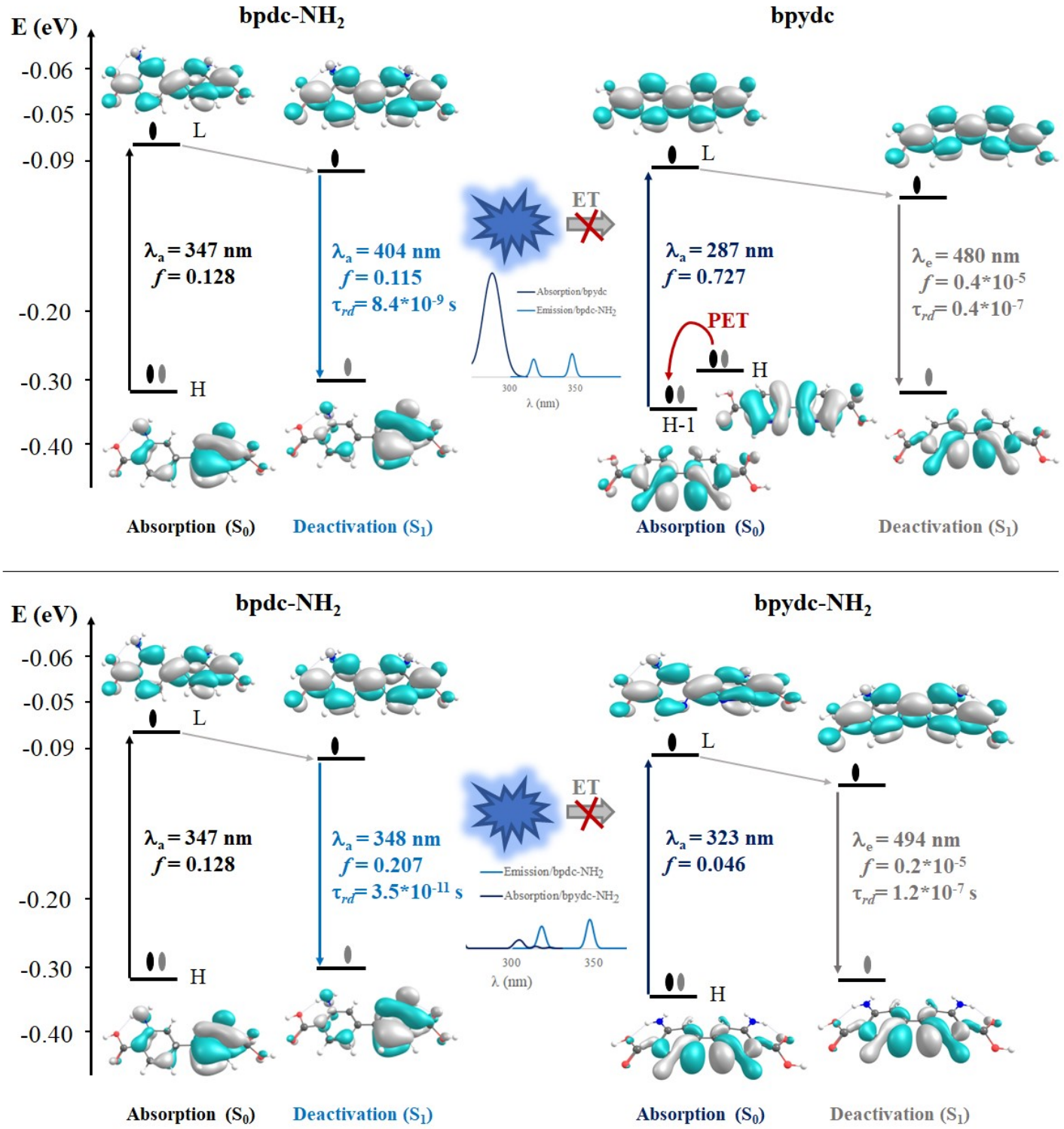


Figure S8. Schematic representation of the photophysical mechanism based on FMOs analysis on the S_0 (absorption) and S_1 states to **bpdc-NH$_2$** and **bpydc-NH$_2$** systems. Where, λ_a and λ_e are the computed wavelength of absorption (black) and deactivation (blue), respectively; *f* is the oscillator strength; τ_{rad} is the radiative transition lifetime and ET is energy transfer. The spectral overlap (emission bpdc/absorption at bpydc) is represented. Isosurface contour values are set as 0.03 with TDDFT/Def2-TZPP/ B3LYP theory level.

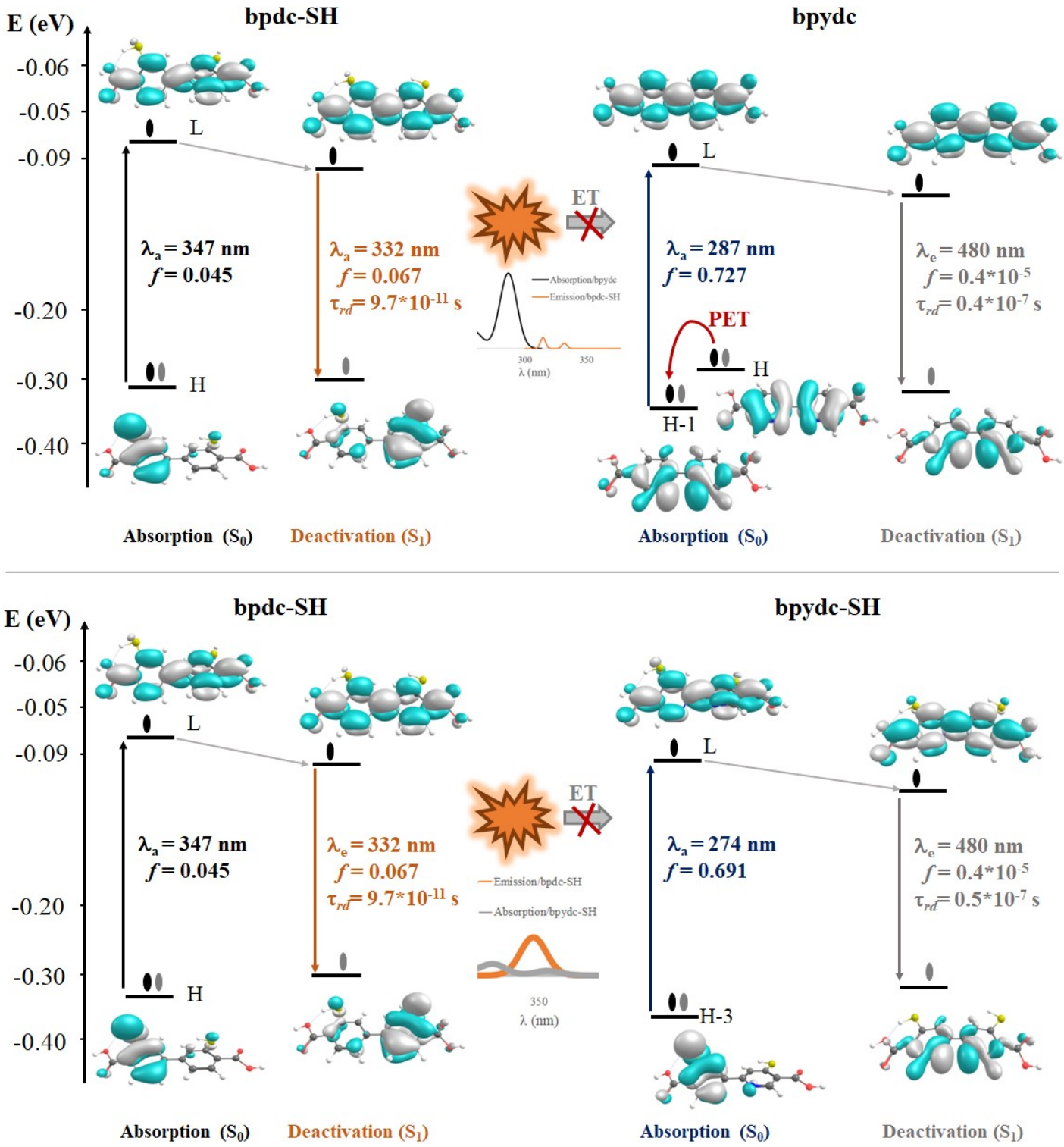


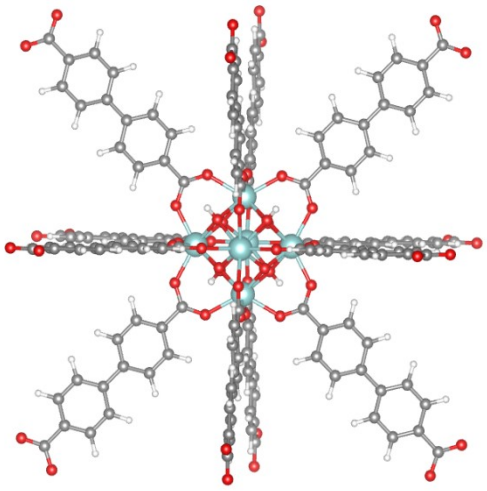
Figure S9. Schematic representation of the photophysical mechanism based on FMOs analysis on the S_0 (absorption) and S_1 states to **bpdc-SH** and **bpydc-SH** systems. Where, λ_a and λ_e are the computed wavelength of absorption (black) and deactivation (blue), respectively; *f* is the oscillator strength; τ_{rad} is the radiative transition lifetime and ET is energy transfer. The spectral overlap (emission bpdc/absorption at bpydc) is represented. Isosurface contour values are set as 0.03 with TDDFT/Def2-TZPP/ B3LYP theory level.

Table S9. First excited singlet and triplet electronic states of the linkers taken from the **1A** and **1A-SH**. All the values are given in cm^{-1}.

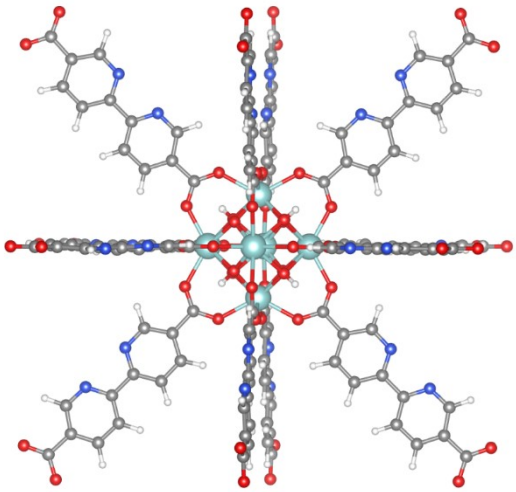
Systems	Linker	State	CASSCF /NEVPT2	Weight	Configuration
1A	bpdc	S_1	31085	89 %	$\pi^2\ \pi^2\ \pi^2 n^1\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
		T_1	28242	91 %	$\pi^2\ \pi^2\ \pi^2 n^1\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
	bpydc	S_1	27205	91%	$\pi^2\ n^2\ n^1\pi^2\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
		T_1	26867	93 %	$\pi^2\ n^2\ n^1\pi^2\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
1A-SH	bpdc-SH	S_1	17721	86 %	$n^1\pi^2\pi^2\pi^2\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
		T_1	17102	87 %	$n^1\pi^2\pi^2\pi^2\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
	bpydc-SH	S_1	24392	91 %	$n^2\pi^2\pi^1\pi^2\ \ \pi^1\pi^0\ \pi^0\ \pi^0$
		T_1	24076	91 %	$n^2\pi^2\pi^1\pi^2\ \ \pi^1\pi^0\ \pi^0\ \pi^0$

Table S10. Morokuma-Ziegler EDA for the systems **1A**, **1A**-(NH_2) and **1A**-(SH), in the S_0. The contribution of the NOCV to the total orbital interaction (*k*) is shown. All values are in kcal mol^{-1}.

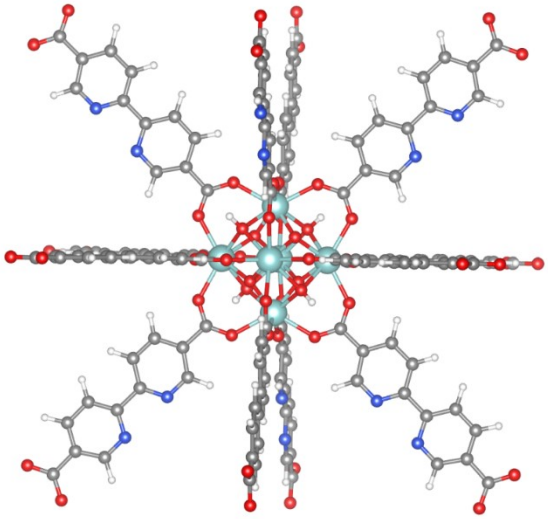
Systems	1A		1A-(NH_2)		1A-(SH)	
	Node-bpdc	**Node-bpydc**	**Node-bpdc-NH_2**	**Node-bpydc-NH_2**	**Node-bpdc-SH**	**Node-bpydc-SH**
ΔE_{Int}	-168.9	-166.37	-170.28	-167.7	-181.75	-188.76
ΔE_{Pauli}	110.0	121.3	112.28	135.4	116.09	167.07
ΔE_{Elect}	-192.8 (69%)	-196.4 (68%)	-197.0 (67%)	-201.6 (67%)	-180.9 (68%)	-228.0 (65%)
ΔE_{Orb}	-78.0 (31%)	-83.32 (32%)	-96.6 (33%)	-101.5 (33%)	-75.6 (32%)	-111.7 (35%)
k	-20.20	-23.10	-20.53	-23.79	-15.30	-23.4



UiO-67 (1)



UiO-67-BPYDC



UiO-67-BPDC- BPYDC (1A)

Figure S10. Optimized structures of UiO-67 via gradient generalized Perdew-Burke-Ernzerhof (PBE) functional, sampling the first Brillouin zone with a 3x3x3 Monkhorst-Pack k-point scheme. Moreover, a 5x5x5 k-point grid scheme was employed for final single energy calculations (including the density of state and bands calculations) with a hybrid HSE06 functional.

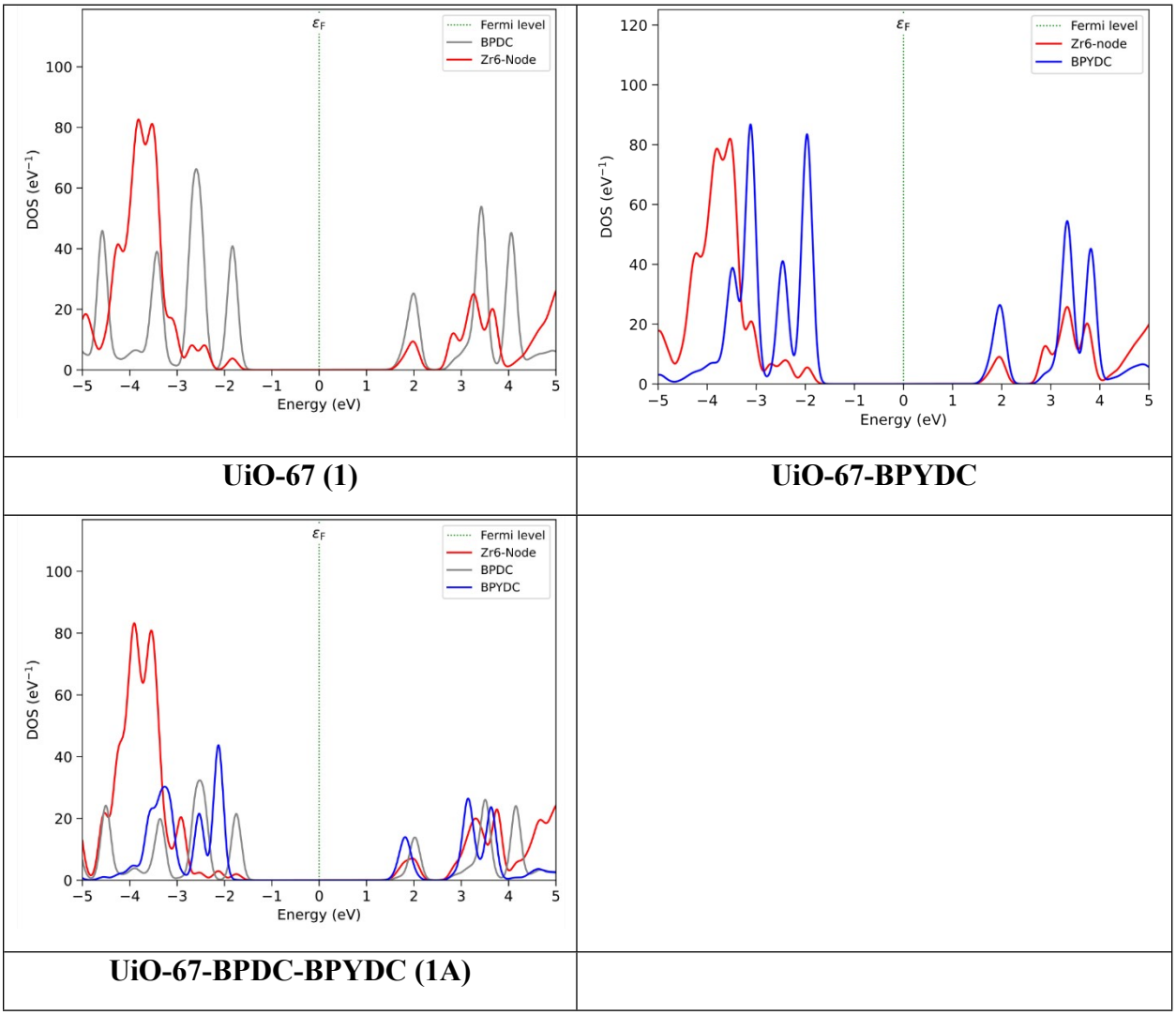


Figure S11: Projected Density of States (PDOS), categorized as Zr6-Node and BPDC, BPYDC. (Zr6-Node definition includes COO-)

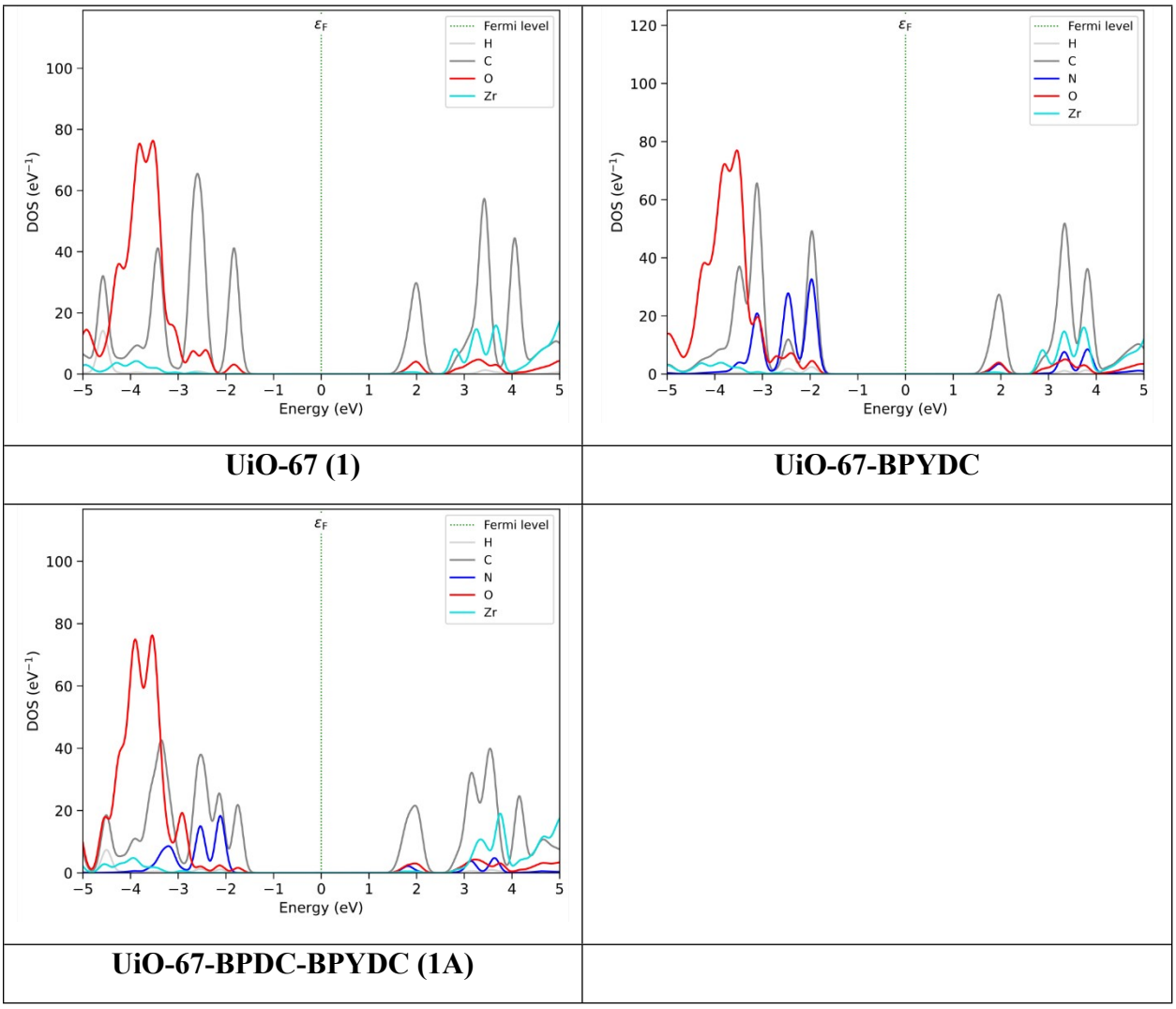


Figure S12: Projected Density of States (PDOS), categorized as elements.

Table S11. Band Gap (experimental data: UiO-67*: 3.68 eV; UiO-67-BPYDC**: 3.36 eV) and Chemical Potential

Structure	Band Gap (eV)	CB (eV)	VB (eV)
UiO-67 (1)	3.418	1.705	-1.713
UiO-67-BPYDC	3.540	1.626	-1.913
UiO-67-BPDC-BPYDC (1A)	3.310	1.584	-1.726

*S. Chavan, J. G. Vitillo, D. Gianolio, O. Zavorotynska,B. Civalleri, S. Jakobsen, M. H. Nilsen, L. Valenzano,C. Lamberti, K. P. Lillerud and S. Bordiga, Phys. Chem Chem. Phys., 2012, 14, 1614

Deming, D. A.; Hurlock, M. J.; Li, X.; Kriegsman, K. W.; Ding, G.; Guo, X.; Zhang, Q. A Facile Method to Introduce Iron Secondary Metal Centers into Metal–Organic Frameworks. *J. Organomet. Chem.* **2019, *897*, 114–119. https://doi.org/10.1016/j.jorganchem.2019.06.037.

Table S12. Description of the optimized structures.

Name	PRIMITIVE CELL_a PBE (Å)	CONVENTIONAL CELL_a (Å)	CELL_angle_ PBE (°)	COD ID_based
UiO-67 with BPDC (1)	19.23	27.19	59.94	4512073
UiO-67-BPYDC UiO-67 with bipyridines. (BPYDC)	19.03	26.91	60.00	7112002
UiO-67-BPDC-BPYDC (1A) UiO-67 alternating BPDC and BPYDC linkers	19.08	26.98	60.12	7112002

*Data values from the experimental crystal structure of UiO-67-bpdc: a=b=c=19.01A (26.88 Å)

**Data values from the experimental crystal structure of UiO-67-bpydc: a=b=c=18.77A (26.54 Å)