Theoretical study of two-photon absorption and fluorescence emission properties of bipyrazine (or hexaazatriphenylene) core based donor- π -acceptor- π -donor framework chromophores

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1 Additional computational details and notes

In this subsection, additional computational details and notes have been provided for better reproducibility. In the Gaussian16 package, the convergence criteria for SCF (RMS density matrix, MAX density matrix and energy) are 1.00×10^{-8} , 1.00×10^{-6} and 1.00×10^{-6} , respectively. The convergence criteria for geometry optimization of ground or excited states (Maximum Force, RMS Force, Maximum Displacement and RMS Displacement) are 0.000450, 0.000300, 0.001800 and 0.001200, respectively. The default ultrafine numerical quadrature grids have been adopted for DFT computations. In the Dalton (2020.0.beta) package, only heavy atoms have been used to create PCM solvation cavity with neglect of hydrogen atoms. The atomic radii used for C, N, O and F are 1.80, 1.65, 1.62 and 1.57 Bohr, respectively. In the FCClasses3 package, the additional parameters for evaluation of the nonradiative internal conversion rate (k_{IC}) from S_1 to S_0 with adiabatic hessian model are: the temperature is 298.15 K, the level broadening function is Gaussian with HWHM (Half Width at Half Maximum) equal to 0.010 eV, and Cartesian coordinates are used for vibrational analysis.

It should be noted that the evaluation of electronic transition dipole moments (M_{ij}) between excited states by the Multiwfn 3.7 program had neglected the relaxation of nuclear charges upon excitation and only taken the contribution from electronic part into account. And the M_{ij} is computed according to the linear response TDDFT excited states transition orbital compositions (coefficient >0.00001). We expect that this approximation could provide relatively reasonable property estimates quickly, and if more accurate results are needed, the interested readers should actually use appropriate quantum chemistry software (e.g. Dalton) to do the calculations.

2 SMILES, shorthand names and chemical structures

of the studied systems

The shorthand names and corresponding canonical SMILES of the studied systems have been given in Table **S1**. And the shorthand names and corresponding chemical structures have been shown in Figure **S1**.

Table S1: The shorthand names and corresponding canonical SMILES of the studied systems.

Shorthand Names	Canonical SMILES
(BOC) ₂ -BPZ	COclccc2c(cl)clcc(OC)ccc1n2-clcnc(-c2cnc(-n3c4ccc(OC)ccc4a4cc(OC)ccc43)cn2)cn1
(BOC) ₂ -BPZ-F	COclccc2c(c1)c1cc(OC)ccc1n2-c1cnc(-c2ncc(-n3c4ccc(OC)ccc4c4cc(OC)ccc43)nc2F)c(F)n1
(BOC) ₂ -BPZ-CN	COclccc2c(cl)clcc(OC)ccc1n2-clcnc(-c2ncc(-n3c4ccc(OC)ccc4c4cc(OC)ccc43)nc2C#N)c(C#N)n1
(BOC-EN) ₂ -BPZ	COclccc2c(c1)c1cc(OC)ccc1n2C=Cc1cnc(-c2cnc(C=Cn3c4ccc(OC)cc4c4cc(OC)ccc43)cn2)cn1
(BOC-EN) ₂ -BPZ-F	COclccc2c(c1)c1cc(OC)ccc1n2C=Cc1cnc(-c2ncc(C=Cn3c4ccc(OC)cc4c4cc(OC)ccc43)nc2F)c(F)n1
(BOC-EN) ₂ -BPZ-CN	COclccc2c(c1)c1cc(OC)ccc1n2C = Cc1cnc(-c2ncc(C = Cn3c4ccc(OC)cc4c4cc(OC)ccc43)nc2C#N)c(C#N)n1
(BOC-EY) ₂ -BPZ	COclccc2c(c1)c1cc(OC)ccc1n2C#Cc1cnc(-c2cnc(C#Cn3c4ccc(OC)cc4c4cc(OC)ccc43)cn2)cn1
(BOC-EY) ₂ -BPZ-F	COclccc2c(c1)c1cc(OC)ccc1n2C#Cc1cnc(-c2ncc(C#Cn3c4ccc(OC)cc4c4cc(OC)ccc43)nc2F)c(F)n1
(BOC-EY) ₂ -BPZ-CN	COclccc2c(c1)c1cc(OC)ccc1n2C#Cc1cnc(-c2ncc(C#Cn3c4ccc(OC)cc4c4cc(OC)ccc43)nc2C#N)c(C#N)n1
(BAC) ₂ -BPZ	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2-c1cnc(-c2cnc(-n3c4ccc(N(C)C)ccc4c4cc(N(C)C)ccc43)cn2)cn1)
(BAC) ₂ -BPZ-F	CN(C)c1ccc2c(c1)c1cc(N(C)C)cccc1n2-c1cnc(-c2ncc(-n3c4ccc(N(C)C)cc4c4cc(N(C)C)ccc43)nc2F)c(F)n1
(BAC) ₂ -BPZ-CN	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2-c1cnc(-c2ncc(-n3c4ccc(N(C)C)ccc4c4cc(N(C)C)ccc43)nc2C#N)c(C#N)n1
(BAC-EN) ₂ -BPZ	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C = Cc1cnc(-c2cnc(C=Cn3c4ccc(N(C)C)cc4c4cc(N(C)C)ccc43)cn2)cn1) + C(C)ccc4cc(N(C)C)ccc4acc(N(C)C)cc4acc(N(C
(BAC-EN) ₂ -BPZ-F	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C = Cc1cnc(-c2ncc(C=Cn3c4ccc(N(C)C)cc4c4cc(N(C)C)ccc43)nc2F)c(F)n1
(BAC-EN) ₂ -BPZ-CN	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C = Cc1cnc(-c2ncc(C=Cn3c4ccc(N(C)C)cc4c4cc(N(C)C)ccc43)nc2C#N)c(C#N)n1
(BAC-EY) ₂ -BPZ	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C#Cc1cnc(-c2cnc(C#Cn3c4ccc(N(C)C)ccc4c4cc(N(C)C)ccc43)cn2)cn1)
(BAC-EY) ₂ -BPZ-F	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C#Cc1cnc(-c2ncc(C#Cn3c4ccc(N(C)C)ccc4c4cc(N(C)C)cccc43)nc2F)c(F)n1
(BAC-EY) ₂ -BPZ-CN	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C#Cc1cnc(-c2ncc(C#Cn3c4ccc(N(C)C)ccc4c4cc(N(C)C)ccc43)nc2C#N)c(C#N)n1
(BAC-EY) ₂ -HAT	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C#Cc1cnc2c3ncc(C#Cn4c5ccc(N(C)C)cc5c5cc(N(C)C)ccc54)nc3c3nccnc3c2n1)
(BAC-EY) ₂ -HAT-CN-i	CN(C)c1ccc2c(c1)c1cc(N(C)C)ccc1n2C#Cc1cnc2c3ncc(C#Cn4c5ccc(N(C)C)cc5c5cc(N(C)C)ccc54)nc3c3nc(C#N)c(C#N)nc3c2n1)c1ccc2c(n2)c1ccc2c(n2)c1ccc2c(n2)c1ccc2n2)c1ccc2n2cc(n2)c1ccc2n2cc2n2)c1ccc2n2cc2n2cc2n2cc2n2
(BAC-EY) ₂ -HAT-CN	CN(C) c1 ccc2 c(c1) c1 cc(N(C)C) ccc1 n2 C # Cc1 nc2 c3 nc cnc3 c3 nc(C # Cn4 c5 ccc(N(C)C) cc5 c5 cc(N(C)C) ccc5 4) c(C # N) nc3 c2 nc1 C # N nc3 c2 nc3 c2 nc1 C # N nc3 c2
(BAC-EY) ₂ -HAT-(CN) ₂	CN(C) c1 cc c2 c(c1) c1 cc (N(C)C) cc c1 n2 C # Cc1 nc 2 c 3 nc (C # N) nc 3 c 3 nc (C # Cn4 c5 cc (N(C)C) cc 5 c5 cc (N(C)C) cc c5 4) c (C # N) nc 3 c 2 nc 1 C # N



(BAC-EY)2-HAT-CN

(BAC-EY)2-HAT-(CN)2

Figure S1: The shorthand names and chemical structures of the studied systems.

3 Solvent effect on maximum two-photon absorption cross-section and excitation energy

The numeric labels, shorthand names and calculated maximum two-photon absorption excitation energy and cross-section of the studied systems in gas and water have been given in Table **S2**. And the calculated maximum two-photon absorption cross-sections and excitation energies in gas, tetrahydrofuran and water have been shown in Figures **S2-S3**. Based on the computed data, we found that from gas to THF and to water, with the increase of solvent polarity, the maximum two-photon absorption cross-section gradually increase uniformly; and that the maximum two-photon absorption excitation energy gradually decrease uniformly (with (BOC-EY)₂-BPZ-F as an exception). Consequently, the relative order of TPA cross-sections across the studied systems should not significantly alter when the used solvent changes.

Table S2: The numeric labels, shorthand names and calculated maximum two-
photon absorption excitation energy and cross-section of the studied systems in
gas and water.

Nos	Shorthand names	in gas		in water	
		E_{max} (eV)	σ_{tpa} (GM)	E_{max} (eV)	σ_{tpa} (GM)
1	$(BOC)_2$ -BPZ	4.32	793	4.28	776
2	$(BOC)_2$ -BPZ-F	4.40	756	4.26	1530
3	$(BAC)_2$ -BPZ-F	4.15	1000	3.92	2010
4	$(BOC)_2$ -BPZ-CN	3.83	992	3.62	1630
5	$(BAC)_2$ -BPZ	3.85	1370	3.74	1640
6	$(BOC-EN)_2$ -BPZ-F	3.79	1370	3.52	2680
7	$(BAC)_2$ -BPZ-CN	3.55	1570	3.23	2750
8	$(BOC-EN)_2-BPZ$	3.82	1830	3.61	3200
9	$(BOC-EY)_2$ -BPZ-CN	3.75	1930	3.46	3390
10	$(BOC-EY)_2$ -BPZ-F	4.59	2060	4.31	3910
11	$(BAC-EN)_2-BPZ-F$	3.57	2120	3.24	4660
12	$(BAC-EY)_2$ -HAT	3.83	1980	3.20	4270
13	$(BOC-EN)_2$ -BPZ-CN	3.66	2160	3.38	4410
14	$(BOC-EY)_2-BPZ$	3.95	2280	3.72	3930
15	(BAC-EY) ₂ -HAT-CN-i	3.52	3670	3.25	5660
16	$(BAC-EN)_2-BPZ$	3.59	2810	3.32	5360
17	$(BAC-EN)_2$ -BPZ-CN	3.40	3270	3.04	7220
18	$(BAC-EY)_2-BPZ-F$	3.65	3230	3.26	6380
19	$(BAC-EY)_2-BPZ-CN$	3.45	4060	3.07	7760
20	$(BAC-EY)_2$ -HAT- $(CN)_2$	3.16	5230	2.95	7710
21	$(BAC-EY)_2-BPZ$	3.68	3870	3.36	7110
22	$(BAC-EY)_2$ -HAT-CN	3.32	5490	3.04	8570



Figure S2: The calculated maximum two-photon absorption cross-sections in gas, tetrahydrofuran and water.



Figure S3: The calculated maximum two-photon absorption excitation energies in gas, tetrahydrofuran and water.

4 The orbital transition characteristics of maximum two-photon absorption excited states for top 8 molecules

The orbital transition characteristics of maximum two-photon absorption excited states for top 8 molecules have been depicted in Figure **S4**.



Figure S4: The orbital transition characteristics of maximum two-photon absorption excited states for top 8 molecules (the values in parentheses give the contribution of dominant orbital transitions).

5 The simulated two-photon absorption spectra for top 8 molecules

The simulated two-photon absorption spectra for top 8 molecules with largest $\overline{\sigma_{tpa}}$ have been depicted in Figure **S5**.



Figure S5: The simulated two-photon absorption spectra for top 8 molecules with largest $\overline{\sigma_{tpa}}$.

6 The ratio of excited energies for top 8 molecules with

largest $\overline{\sigma_{tpa}}$

The maximum TPA excitation energy (E_{max}) , linear absorption excitation energy (E_{abs}) , their difference (D_1) , and relative ratio of energies (R_1) of top 8 molecules have been given in Table **S3**.

Table S3: The maximum TPA excitation energy (E_{max}) , linear absorption excitation energy (E_{abs}) , their difference (D_1) , and relative ratio of energies (R_1) of top 8 molecules.

No.	E_{max}	E_{abs}	$D_1 = E_{max} - E_{abs}$	$R_1 = D_1 / E_{abs}$
	eV	eV	eV	
1	3.34	2.78	0.56	0.20
2	3.40	2.96	0.44	0.15
3	3.14	2.80	0.34	0.12
4	3.36	3.02	0.34	0.11
5	3.18	2.89	0.29	0.10
6	3.02	2.43	0.59	0.24
7	3.46	3.03	0.43	0.14
8	3.13	2.79	0.34	0.12

7 The distribution of Huang-Rhys factor versus frequency for top 8 molecules

The distribution of Huang-Rhys factor $(S_j > 0.1)$ versus frequency for top 8 molecules have been depicted in Figure **S6**.



Figure S6: distribution of Huang-Rhys factor versus frequency for top 8 molecules (only $S_j > 0.1$ are shown).