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# Molecular and Electronic Structure and Properties of the Single Benzene-Based Fluorophores Containing Guanidine Subunit

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## ABSTRACT

The Gibbs energies of protonation ( $\Delta G_p$ ) and the basic photophysical properties for single-benzene fluorophores (SBFs) containing guanidine and/or amino subunits and the changes that occur upon protonation were modeled by the TDDFT approach. The calculated  $\Delta G_p$  energies for amino SBFs in the S<sub>1</sub> state range from 985 to  $1100 \, \text{kJ} \, \text{mol}^{-1}$  which are below the values for guanidines. The protonation of the guanidine-SBFs induces a hypsochromic shift of the absorption and the emission maxima with the Stokes shift of > 100 nm in both cases. Isomerization through the ESIPT process is less probable than in amino-SBFs due to the unfavorable thermodynamics. Still, if it occurs, it leads to a strong red shift of the emission by > 150 nm. Aromaticity indices point to strong antiaromatic character of the examined guanidino-SBFs in the FC region which decreases upon geometrical relaxation and ESIPT. The excited state proton transfer occurs in guanidine-SBF/phenol complexes in the S<sub>1</sub> state, stabilizing CT states and fluorescence quenching.

# 1 | Introduction

Fluorescence emission in the visible part of the electromagnetic spectrum is nowadays a hot topic and is suggested as an excellent feature of biologically interesting molecules as well as for application in various branches of material sciences [1, 2]. Among various photo-emissive systems, single-benzene-based fluorophores (SBFs) attracted much attention due to their low molecular weight, simplicity of synthesis, and tunability [3]. Depending on the substitution pattern, SBFs show interesting mechanochromic [4] or sensing properties [5], which can be used as the turn-on fluorescent probes [6], and for cellular imaging [7], whereas their tendency to form flexible crystals [8] can be used for the construction of 3D optical waveguides [9]. By proper design, the fluorescence of the SBFs can be shifted to the NIR region, which is interesting for biosensing and bioimaging applications [10–12]. Although known for more than 100 years [13], terephthalatebased SBFs together with other structurally analogous systems regained the special attention of the scientists in the last 20-30 years. Controlling the electron density on the amino group(s) proved crucial for achieving the desired optical/electronic properties of 2,5-diaminoterephthalates as recently shown by Bao et al. [14]. The electronic structure of the SBFs was investigated in detail and the origin of the efficient fluorescence and the large Stokes shift have been discussed [3]. Two crucial features determine the properties of SBFs: (1) accessibility of the charge transfer state within the single benzene ring and (2) stabilization of the  $S_1$  state below the conical intersection. The latter was initially attributed to alleviating the antiaromaticity through geometry relaxation [15-17]. However, a detailed analysis of the electronic structure and application of the aromaticity indices (AI) based on the RBSO analysis dispute

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this and suggest that the stabilization of the  $S_1$  state is primarily due to the X motif of substitution [18].

In general, fluorescent systems equipped with guanidine functionality have great potential as sensors for the anions or polar groups [19]. In previous papers, we have shown that guanidines do significantly change the spectroscopic properties of small chromophores but the effect is reduced strongly as the size of the chromophore increases [20, 21]. Also, the effect of the protonation on the small molecular systems is noticeable and we were able to construct a system that switches between colored and colorless and back upon protonation/deprotonation processes [19]. Additionally, due to the inherent basicity significantly higher than that of anilines, the guanidine subunit is expected to undergo protonation under much milder conditions than those described recently (5-fold excess of TFA) [14]. Having all this in mind, we envisioned that the SBFs-guanidine systems have great potential as novel photoactive systems highly sensitive to protonation.

Herein, we present the results of the computational investigations of the guanidine-SBF systems 1 and 2 (Figure 1) with an emphasis on the role of protonation on the change in the selected excited state properties. In the case of cyclic guanidine 2, we considered two chemically non-equivalent tautomers with endocyclic imino position  $(2_{N1})$  and exocyclic imino position  $(2_{N2})$ . The results are supplemented with the computed data for the series of known amine-SBFs and their protonated forms. In particular, terephthalate and 4-acetylacetophenone derivatives were selected due to the relatively large amount of experimental data available. The purpose of these calculations is twofold. First, comparison with experiments provides the accuracy of the employed computational method and its applicability to the investigated systems. Second, it allows a detailed comparison of excited state properties of known SBFs with novel guanidine model systems.

#### 2 | Methods

All calculations were performed using the Gaussian16 program package [22]. Geometry optimizations were done using M06-2X density functional [23] in combination with a 6-31G(d) basis set assuming chloroform as a solvent. Calculated minima were verified by vibrational analysis showing imaginary frequencies (NImag=0). For calculating Gibbs energies of protonation in the S<sub>0</sub> and S<sub>1</sub> states, electronic energies were improved at the M06-2X(CHCl<sub>3</sub>)/6-311++G(2df,2pd) level of theory. The solvent was modeled as the dielectric continuum employing the SMD approach [24] with default parameters implemented in the Gaussian16 program package. The excited state calculations

were conducted by TD-DFT approach (nstate = 5, root = 1) employing either PBE0/6-31G(d) [25] or CAM-B3LYP/6-31G(d) [26] density functionals. A romaticity indices were determined for the S<sub>o</sub> or S<sub>1</sub> wavefunctions calculated at CASSCF(14,12)/6-31G(d) (for neutral or O-protonated structures) or CASSCF(12,11)/6-31G(d) (for N-protonated structures) levels of theory employing the Dalton 2020.1 program package [27, 28]. CASSCF calculations were performed at the M06-2X optimized geometries assuming the gas-phase environment. The MCI [29] aromaticity indices and other electronic (anti)aromaticity descriptors (FLU [30] and AV1245 [31]) were computed using Multiwfn 3.8 software [32]. In the case of MCI indices, an option iMCBOtype was set to 1. For the calculation of FLU indices, the DI(C-C) value was set to 1.386 as obtained for benzene using the CASSCF(6,6)/6-31G(d) approach. The NICS(1)<sub>zz</sub> [33] values as the magnetic aromaticity indices were obtained by Dalton 2020.1 program as well. Visualization of the geometries and orbitals was done by Molden 6.9 [34, 35]. The second-order stabilization interaction  $(E_{ii}^{(2)})$  and the destabilization energies due to the orbital deletion were calculated by the NBO 3.1 routine [36] implemented in the Gaussian16 program package.

## 3 | Results

Besides on guanidine-SBFs (Figure 1), calculations of the excited state properties were conducted on two groups of the amine-SBFs-terephthalate-based (TA, 3-12, Figure 2) and 4-acetylacetophenone (AAP, 13-19, Figure 2) based SBFs. The lowest energy excitation in SBFs was considered to have intramolecular charge transfer character [37] by some authors, but this is also questioned by others [16]. Therefore, we tested the performance of PBE0 and CAM-B3LYP functionals for the calculation of absorption and emission energies on top of the M06- $2X(SMD = CHCl_{2})/6-31G(d)$  optimized geometries. The PBE0 functional was successfully used previously [19] and it was shown that it works better for local excitations (LE) than CAM-B3LYP. Also, its performance is highly dependent on the orbital overlap [19, 38]. On the other hand, CAM-B3LYP is expected to perform similarly for LE and CT states [33]. The accuracy of these functionals varies strongly depending on the system in question and often they provide good results by the cancelation of the errors [39]. Therefore, we decided to test their performance on the set of known amino-SBFs [16, 40, 41] (Figure 2). Since most of the experimental data refer to the measurements in chloroform solution, the same solvent was also used in the calculations. The correlation between the computed and experimental data is given in Figure 3.

The results for PBE0 functional indicate very good agreement within emission and absorption data themselves with



FIGURE 1 | Structures of the guanidine substituted SBFs. Enumeration of the guanidine nitrogen atoms used throughout the text is also given.



FIGURE 2 | Structures of the amino-SBFs used for correlation.



**FIGURE3** | Correlation between computed and measured absorption ( $\lambda_{Abs}$ ) and emission ( $\lambda_{Em}$ ) maxima for the series of amine-SBFs. Computations were performed using PBE0 (a) and CAM-B3LYP (b) functionals. The number associated with each data point indicates the compound numbering scheme in Figure 2.

quite satisfactory overall correlation coefficient (0.9776, see Figure 3a). It should be noted that the largest off-liners are phenyl and 3,5-*bis*(trifluoromethyl)phenyl derivatives **8** and **9** (emission

data). Absolute  $\Delta \lambda_{\rm Abs}$  and  $\Delta \lambda_{\rm Em}$  values are within 20 nm. On the other hand, CAM-B3LYP(SMD)/6-31G(d)//M06-2X(SMD)/6-31G(d) provides slightly better estimates of  $\lambda_{\rm Em}$  for amino-SBFs

8 and 9 but it does not reflect on the overall quality of the correlation ( $r^2 = 0.973$ ) which is practically the same as the one obtained by PBE0 functional. If only absorption energies are taken into account, the correlation between calculated and experimental  $\lambda_{Abs}$  is excellent ( $r^2 = 0.995$ ) implying a significant difference in the accuracy of the  $\lambda_{Abs}$  and  $\lambda_{Em}$  estimates. It seems that absorption and emission energies do not fit the same correlation (see Figure 3b). Additionally, it should be noted that the slope of the correlation line obtained by CAM-B3LYP deviates significantly from the ideal value of 1.0, while the same parameter is practically ideal when PBE0 functional is used. Besides that, the  $\lambda_{Abs}$ and  $\lambda_{\text{Fm}}$  values calculated by CAM-B3LYP are underestimated by 22-65 nm from the experimental values with the systematic mean signed error (MSE) value of -48nm. The MSE value for the PBE0 data is better and amounts -3.1 nm. Despite the mentioned off-liners, the PBE0 computational model was considered the better choice and it was used to estimate the basic optical properties of guanidine-SBFs and their protonated forms.

The calculated emission wavelengths from the S<sub>1</sub> state for the considered guanidines 1 and 2 fall in the range of 525–541 nm which is lower than the values obtained for the alkyl- and arylamino-SBFs (3–9;  $\lambda_{\rm Em}$ =558–606 nm) but higher than those obtained for the acylated derivatives 10–12 ( $\lambda_{\rm Em}$ =450–456 nm). The same trend also holds for the absorption data (see Table S1). Increased absorption energy in 2<sub>N2</sub> and 2<sub>N1</sub> relative to the diamine 3 and other alkylamino analogues is not surprising since in both tautomers one can expect the decreased overlap between guanidine orbitals and the  $\pi$ -system of the chromophore (Section S3). Additionally, full planarization of the system takes place in 2<sub>N1</sub>, whereas in 2<sub>N2</sub> the guanidine moiety enforces twisted geometry [20]. Irrespective of the conformation, overlap between the aromatic ring and the adjacent amino atom is decreased relative to the amine derivatives, and consequently,

the HOMO-LUMO gap ( $\Delta E_{\rm HI}$ ) is increased (Figure 4, see Section S3).

Besides the difference in the junction C–N bond length, (Figure 4) NBO analysis of the FMOs in  $\mathbf{2}_{N1}$  and  $\mathbf{2}_{N2}$  (Figure 5) indicates stronger  $\pi$  (or pseudo  $\pi$ ) overlap in  $\mathbf{2}_{N1}$  corroborated by significantly higher  $E_{ij}^{(2)}$  value ( $E_{ij}^{(2)}$  = second order stabilization energy between the donor and the acceptor orbitals within the framework of NBO theory).

## 3.1 | Protonation of the SBFs

The protonation of the bases usually leads to the blue shift of the lowest energy band in the UV spectra of amino and guanidinosubstituted chromophores [19, 20, 42]. In the context of SBFs, the influence of protonation is rarely discussed in the literature [14, 43]. Upon protonation, the strong hypsochromic effect in fluorescence for the methylamino-SBF **4** was observed while in the case of the phenylamino derivative **8**, complete quenching of the fluorescence took place [14]. Similarly, the *N*-methylated analogue of **4** shows dual emission in water (at 485 and 608 nm) which originates from the mixture of the protonated and non-protonated species in water [38]. Again, a strong hypsochromic shift was induced by protonation.

To get insight into the origin of these changes, we optimized the protonated structures in the  $S_1$  state. For each of these two ammonium-SBF cations (**4H**<sup>+</sup> and **8H**<sup>+</sup>), two minima were identified in the excited state (*N*-protonated and *O*protonated). The latter was achieved by the excited state intramolecular proton transfer (ESIPT) from the protonated nitrogen atom to one of the EWG substituents. ESIPT is a well-known photochemical process that can trigger dual-band



**FIGURE 4** + Side view of  $2_{N1}$  (left) and  $2_{N2}$  (center) and 3 (right). The torsional angle between the benzene and guanidine planes in  $2_{N1}$  and  $2_{N2}$  are 1.7° and 74°, respectively. Selected distances are in Å. Parenthesized values refer to the  $S_1$  state.



**FIGURE 5** | Frontier orbitals in  $\mathbf{2}_{N1}$  and  $\mathbf{2}_{N2}$ .  $E_{ij}^{(2)}$  is given for the  $n(\pi) \rightarrow \pi^*$  interaction across the guanidine-SBF junction (N–C) bond in the framework of NBO theory (1 kcal = 4.184 kJ).

fluorescence as recently shown by Kim et al. [44]. Calculated  $\lambda_{\rm Em}$  for **4H**<sup>+</sup> (*N*-protonated structure) of 449 nm is 21 nm lower than the experimental one 470 nm, measured in the solid state [14]. Since the emission of SBFs in the solid state is red-shifted relative to the solution as generally observed by others [14, 36], our results fit the data quite well. The second minimum at the S<sub>1</sub> PES was located for the O-protonated tautomer  $4H_{nt}^+$ with the calculated  $\lambda_{\rm Em}$  of 747 nm which is close to the visible/NIR border. Similarly, calculated  $\lambda_{\rm Em}$  for the *N*-protonated and O-protonated 8H+ amounts 628 and 844 nm, respectively. The latter value implies a shift of the fluorescence outside the visible region upon ESIPT which could be one of the reasons for the observed fluorescence quenching. On the other hand, such a low  $S_1/S_0$  energy gap can also indicate the proximity of the conical intersection (CI) which would also lead to the fluorescence quenching by non-radiative relaxation to the ground state. Identification of possible CI is beyond the scope of this paper and was not pursued. Here, we should emphasize that no significant decrease in the oscillator strengths for the corresponding transitions was calculated.

These results triggered us to optimize both minima for other protonated structures and to examine the relation between the basicities of the examined SBFs in the ground and the first excited state and the emission maxima. The results are summarized in Table 1. The Gibbs energies of protonation in chloroform ( $\Delta G_p$ ) were taken as a measure of the basicity. The derivatives **10–12** as well as **17–19** were omitted from this analysis due to the low basicity of the amide, urea, and carbamate nitrogen atoms.

In most investigated structures, a drop in the  $\Delta G_{\rm p}$  upon excitation was observed which is consistent with previous knowledge about photoacidity of anilines [45-48]. The exception is the derivative **9** where the increase in  $\Delta G_n$  on going to the  $S_1$  state is calculated. A comparison of the calculated data indicates a much stronger effect in the series of terephthalates 3-8 (TA series) than for 4-acetylacetophenone derivatives 13-16 (AAP series). Isomerization to the O-protonated forms by intramolecular proton transfer leads to the stabilization of the systems in both sets of amino-SBFs (Table S4). A comparison of two diamino analogues (3 and 13) against the reference 1,4-diaminobenzene (DAB) indicates a similar effect of the electron-withdrawing groups in the ground state but a markedly different one in the S<sub>1</sub> state. Calculated adiabatic S<sub>1</sub>–S<sub>0</sub> energy differences for **3**, **13**, and **DAB** are 258, 238, and 357 kJ mol<sup>-1</sup>, respectively (Table S5b). The corresponding differences in the protonated forms amount to 329, 319, and 409 kJ mol<sup>-1</sup> for 3H<sup>+</sup>, 13H<sup>+</sup>, and DABH<sup>+</sup>, respectively (Table S5b). The results indicate stronger stabilization of the S<sub>1</sub> state by acetyl group than one with the ester group irrespectively of the protonation state but the effect is more pronounced for neutral structures. As a consequence, a decreased  $\Delta G_{\rm p}^{*}$  relative to **DAB** was obtained being larger for the diacetyl derivative 13 than for 3. Besides having a stronger stabilization effect on the S<sub>1</sub> state than the ester group, the acetyl group also acts as the stronger base during the ESIPT as evidenced by a larger increase in  $\Delta G_{\rm p}^{*}(13)$  relative to  $\Delta G_{\rm p}^{*}(3)$  upon ESIPT (Table 1). In line with that, the difference in energies between the N- and O-protonated forms is smaller in the TA series than in the AAP series. Additionally, in the TA series, the difference

 TABLE 1
 Calculated Gibbs energies of protonation in chloroform for all investigated SBFs.<sup>a</sup>

				SBF	SBFH <sup>+</sup>	SBFH <sup>+</sup> (PT)
SBF	$\Delta G_{\rm p}({\rm SBF})$	$\Delta G_{\rm p}^{*}({\rm SBF})$	$\Delta G_{p}^{*}(\text{SBF, ESIPT})$	$\lambda_{\rm Em}/{\rm nm}$	$\lambda_{\rm Em}/{\rm nm}$	$\lambda_{\rm Em}/{\rm nm}$
1	1192	1164	1156	540.6	477.7	645.7
2 <sub>N1</sub>	1171	1141	1048	524.6	469.7	774.3
2 <sub>N2</sub>	1175	1152	1152	539.7	469.7	646.4
3	1096	1025	1050	555.6	412.6	686.7
4	1105	1039	1053	593.5	448.7	746.7
5	1112	1047	1056	594.8	450.4	753.1
6	1120	1057	1062	600.6	455.0	764.7
7	1114	1059	1058	605.6	463.3	784.7
8	1063	1041	1056	596.5	627.9	844.3
9	979	985	1029	557.7	540.9	753.2
13	1095	1014	1086	618.4	n/c <sup>b</sup>	877.4
14	1078	1022	1071	575.1		764.6
15	1072	1028	1067	555.6		718.4
16	1067	1023	1065	553.2		705.7
DAB <sup>c</sup>	1097	1045	_	339.7	291.8	

<sup>a</sup>All  $\Delta G_{\rm p}$  are in kJ mol<sup>-1</sup>.

 ${}^{b}n/c = n^{P}$  calculated due to the large difference in stability of two minima in the S<sub>1</sub> state.

<sup>c</sup>**DAB**=1,4-diaminobenzene.

TABLE 2 | Calculated aromaticity indices (MCI and NICS(1)<sub>zz</sub>) for the selected guanidine- and amine-SBFs in the ground and the S<sub>1</sub> state.<sup>a</sup>

SBF	S <sub>0</sub> @S <sub>0</sub>	S <sub>1</sub> @S <sub>0</sub>	S <sub>1</sub> @S <sub>1</sub>	S <sub>0</sub> @S <sub>1</sub>	S <sub>1</sub> @S <sub>1</sub> (PT)	S <sub>0</sub> @S <sub>1</sub> (PT)
1	3.93 (-21.9)	0.76 (47.7)	0.89 (23.0)	3.40 (-19.1)		
$1 H^+$	3.84 (-21.2)	0.82 (51.6)	0.89 (29.4)	3.53 (-19.2)	1.79 (3.4)	3.43 (-19.3)
2 <sub>N2</sub>	4.01 (-22.3)	0.74 (50.7)	0.86 (25.5)	3.43 (-19.3)		
$2_{N2}H^+$	3.76 (-21.3) <sup>b</sup>	0.83 (54.3) <sup>b</sup>	0.89 (30.6) <sup>b</sup>	3.51 (-19.4) <sup>b</sup>	1.86 (2.5)	3.55 (-20.0)
4	3.67 (-21.5)	0.91 (34.3)	0.99 (17.6)	3.25 (-19.3)		
4H <sup>+</sup>	3.62 (-20.9)	1.21 (33.5)	1.26 (13.2)	3.50 (-19.6)	2.45 (-11.6)	3.17 (-19.1)
Benzene	5.34 (-27.2)	0.49 (92.9)	0.46 (79.2)	5.09 (-25.7)		

<sup>a</sup>The calculated MCI values are multiplied by 100, the NICS(1)<sub>77</sub> indices are given in parentheses.

<sup>b</sup>Structures and aromaticity indices are identical as for  $2_{N1}H^+$  (Figure 6b).



**FIGURE 6** | (a) MCI × 100 and NICS(1)<sub>zz</sub> (in parentheses) values calculated for the  $\mathbf{2}_{N1}$  in the ground and the S<sub>1</sub> state. (b) MCI × 100 and NICS(1)<sub>zz</sub> (in parentheses) values calculated for the  $\mathbf{2}_{N1}$  H<sup>+</sup> in the ground and the S<sub>1</sub> state.

in energies of two minima at the  $S_1$  PES decreases with the increased electron-donating ability of the substituent. Given that the emission wavelength from these two minima is expected to be markedly different (Table 1), tuning the electron density on the protonated center could lead to the dual-emitting systems triggered by protonation/ESIPT.

The tabulated data also show a smaller impact of the excitation on the basicity of the guanidine derivatives with respect to amino derivatives. *N*-protonated structures remain either more stable  $(2_{N1})$  or as stable as the *O*-protonated isomer  $(1 \text{ and } 2_{N2})$ . A relatively small decrease in the basicity of guanidine-SBFs could be ascribed to the high intrinsic basicity of the guanidine

subunit as a consequence of the efficient charge stabilization [49] which, in turn, is less affected by the changes in the electronic structure of the aromatic subunit (see the next section). The similarity of the properties of 1 and  $2_{N2}$  is not surprising due to the similar orientation of the guanidine subunit. Guanidine  $\mathbf{2}_{N1}$  shows the largest change in the basicity and this could be ascribed to the endocyclic position of the imino nitrogen atom (the most basic site in the S<sub>0</sub> state). Protonation of the guanidine subunit leads to the decrease in  $\pi$ -overlap across the junction C-N2 bond, (Figure 5; for the guanidine nitrogen atoms numbering scheme see Figure 1), and cleavage of the  $N1-HC_{Ar}$  intramolecular hydrogen bond. These effects lead to the formation of the protonated form identical to  $2_{N2}H^+$ . Excitation to the S<sub>1</sub> state removes the unfavorable interaction in the HOMO of the neutral base and the difference between two tautomers of the base 2 becomes more pronounced on account of the more efficient stabilization of the neutral base  $2_{N1}$ .

The O-protonated minimum for the  $2_{N1}$  isomer needs some comments. In this case, a proton transfer from the  $N^1$  (endocyclic) position to the neighboring ester oxygen atom is assumed. Intramolecular proton transfer in the S<sub>1</sub> state did not provide a hydrogen-bonded O-protonated minimum but the proton spontaneously went back to the guanidine subunit. Comparison of the calculated  $\Delta G_p^*$  associated with *N*- and *O*-protonation in the S<sub>1</sub> state (**2**<sub>N1</sub>**H**<sup>+</sup> and **2**<sub>N1</sub>**H**<sup>+</sup>(PT) structures) indicated quite a large differences in their Gibbs energies amounting to almost 100 kJ mol<sup>-1</sup> (ca 1 eV). That implies the possibility of the ESIPT process only under higher energy conditions and most likely after the excitation to the higher states. The calculated reaction profile for this path (Section S4) indicates that ESIPT is thermodynamically controlled and that the O-protonated form exists as a very shallow minimum at the S1 PES and highly energetic species in the S<sub>0</sub> state (147 kJ mol<sup>-1</sup> above N-protonated structure). Nevertheless, for the completeness of the calculated data, we did not neglect this structure.

# 3.2 | Antiaromaticity Relief in Guanidine-SBFs

As a next step, a change in aromaticity of the examined guanidine-SBFs and their protonated forms was analyzed. It has been shown that the change in the acid/base properties in the  $S_1$  state is closely related to the antiaromaticity relief [41]. For this purpose, we calculated MCI aromaticity indices (AI) which are based on the (de)localization of the electron density within the considered ring system and the  $\mathrm{NICS(1)}_{\mathrm{zz}}$  which was taken as the magnetic aromaticity index. Although the NICS indices are widely used, the MCI is considered to be the most reliable aromaticity descriptor [50]. Namely, NICS and magnetic aromaticity descriptors in general tend to exaggerate (anti)aromatic character when compared to results from nonmagnetic descriptors [51, 52]. Also, molecules with several substituents containing heteroatoms might be prone to exhibit the local circulations in the current density that might trigger false (anti)aromaticity assessments (e.g., see Reference [53]). Calculation of AIs was conducted for the S<sub>0</sub> and S<sub>1</sub> state in the FC point as well as at the geometry corresponding to the S<sub>1</sub> minimum. As the reference structure, the MCI and  $\text{NICS(1)}_{zz}$  data for benzene were added (Table 2 and Figure 7). These data represent a limiting values for excited state antiaromaticity.

The changes in the AI for the neutral  $2_{N1}$  and its protonated form are shown in Figure 6, while the corresponding results for **1**,  $2_{N2}$ , and **4** are given in Table 2. Also, the correlation between MCI and NICS(1)<sub>zz</sub> aromaticity indices for all calculated structures at the S<sub>0</sub> and S<sub>1</sub> PESs are given in Figure 7. Additionally, AV1245 and FLU indices were calculated as well and the results are shown in Figure S2.

As shown in Figure 7, the data obtained for amine and guanidine SBFs fall in between the values obtained for benzene. MCI indices follow the same trend as  $NICS(1)_{zz}$  although the correlation is not linear. The results, somewhat unexpectedly, predict a slight decrease in the MCI for S<sub>1</sub>@S<sub>0</sub> state on going from amine derivative 4 to the guanidines 1 and  $2_{N2}$ . (MCI values are decreased from 0.91 (4) to 0.76 (1) and 0.74 ( $2_{N2}$ )). It appears that weakening the N- $\pi$  interactions increases antiaromaticity in these systems. The systems still have pronounced antiaromatic character after the geometrical relaxation in the excited state. The same holds also for the protonated species, but in these cases, antiaromaticity is further decreased by ESIPT. According to the  $NICS(1)_{77}$ data, formed O-protonated structures possess a non-aromatic character in the case of guanidinium ions  $1H^+$  and  $2_{N2}H^+$ , however in the case of  $2_{N1}H^+$  and  $4H^+$ , the O-protonated structure becomes aromatic. The same conclusion could be drawn from MCI indices if we assume the range of 0.015-0.020 as the typical values for nonaromatic structures (Figure 7). Such aromaticitygenerating ESIPT has been observed earlier by Plasser and coworkers in a series of cyclobutadiene derivatives [54]. A comparison of the data for neutral and protonated species indicates a negligible effect of the protonation on the (anti)aromaticity in the S<sub>0</sub> state, whereas the changes are more pronounced in the S<sub>1</sub> state but follows the same trend.

A difference in trends between MCI and NICS data was observed only for the protonation-induced changes in the (anti)aromaticity for  $S_1@S_0$  and  $S_1@S_1$  states in guanidine and amine structures. MCI indices suggest an increase in antiaromaticity upon protonation in all structures, while the NICS(1)<sub>zz</sub> values show the same trend for guanidines and the opposite trend for **4**. Nevertheless, the differences are still small in all cases and





should not be considered as relevant. Overall, the trends indicate higher consistency of the MCI data than  $NICS(1)_{77}$ .

Of other aromaticity indices, the comparison of AV1245 with NICS shows a similar trend as MCI against NICS indices but with a larger scattering of points (Figure S2). The poorest correlation was obtained for FLU indices which is most likely due to the combination of the neutral and protonated structures (Figure S2). FLU indices also show the opposite trend along the S<sub>1</sub> geometry relaxation path indicating an increase in the antiaromatic character on going from FC geometry to the S1 minimum. On the other hand, the changes in FLU indices caused by intramolecular proton transfer are consistent with NICS and MCI data (Section S6, Table S8).

# 3.3 | Intermolecular Complexes of Guanidine-SBFs

As noted in the Introduction section, some SBFs form flexible crystals or possess other interesting features in the solid state [4, 8, 9]. Construction of the proton donor-acceptor (PDA) system that could switch from the neutral-neutral to the salt-bridged non-covalently bound heterodimers can provide an additional dimension of the applicability of the SBFs. Driven by this idea. we modeled selected PDA systems in which guanidine-SBF plays the role of the proton acceptor while the donor is phenol or its para-substituted derivative. The phenols were chosen because of their relatively low pK<sub>a</sub>s in the ground state (GS), comparable to the protonated aromatic guanidines. Additionally, phenols are well-known photoacids [55] with highly increased acidity in the S<sub>1</sub> state which may ensure efficient proton transfer to the guanidine subunit. Three phenols bearing substituents with different electronic effects were taken into consideration (P1-P3, Figure 8) since they differ strongly in the  $pK_{a}$  [56] and show a tendency for  $\pi$ - $\pi$  stacking [57, 58].

For each guanidine and phenol pair, the PDA complexes were constructed by assuming a non-covalent binding between the components via H-bond, either as non-stacked hydrogenbonded (HB-type, complexes denoted by **a** and **b**) or  $\pi$ -stacked ( $\pi$ -type, complexes denoted by **c** and **d**, see Figure 8) structures. Additionally, each complex can show two minima associated with the proton movement across the HB interaction: neutral (denoted by **a** in HB structures and **c** in  $\pi$ -stacked structures) and zwitterionic (denoted by **b** in HB structures and **d** in  $\pi$ stacked structures) before and after proton transfer, respectively. In the case of guanidine-SBF 1, phenol interaction can be directed to the N2 position only (20a-d-22a-d). In the case of 2, two possibilities were examined: binding to N1 (23a-d-25a-d) or N2 (26a-d-28a-d). A schematic representation of the possible structures is shown in Figure 8.

The ground state calculations indicate that the proton transfer from phenols to guanidines within complexes is not the preferred process. In complexes with P1 and P2 phenols, only neutral a and c-type structures were successfully optimized. Attempts to optimize zwitterionic **b** and **d** minima resulted in back proton transfer during optimization. In the case of P3, two minima on the proton transfer reaction coordinate are located but neutral forms are more stable relative to the zwitterionic in both HB and  $\pi$  complexes. The  $\pi$  complex **25c** is more stable than the corresponding non-stacked (HB) 25a form by 7.9 kJ mol<sup>-1</sup> (Table 3) indicating a significant effect of the  $\pi$ -stacking in the case of phenol containing strong electron withdrawing group (P3). The employed method also predicts higher energies of the complexes



hydrogen-bonded (HB) complexes

FIGURE 8 | Modes of the binding of phenols to the guanidine-SBFs.



<b>TABLE 3</b>   Calculated relative Gibbs energies ( $\Delta G_{rel}$ ), estimated					
$\lambda_{\rm Em}$ and the corresponding oscillator strengths $(f_{\rm osc})$ in the $\rm S_1$ state					
calculated for two minima along the proton transfer coordinate within					
the $\pi$ -complexes between the guanidine SBFs and phenols <b>P1–P3</b> . <sup>a</sup>					

	Ground state S <sub>0</sub>	Excited state S <sub>1</sub>		
Structure <sup>b</sup>	$\Delta G_{ m rel}/$ kJ mol <sup>-1</sup>	$\Delta G_{ m rel}/ m kJmol^{-1}$	$\lambda_{\rm Em}/{\rm nm}$	$f_{ m osc}$
20c	12.2	10.7	598	0.135
20d	Back PT	-12.1	1768	0.001
21c	7.8	6.1	590	0.135
21d	Back PT	-35.4	8523	0.000
22c	27.6	-15.6	1420	0.002
22d	29.0	-1.3	876	0.003
23c	-1.5	0.4	529	0.146
23d	Back PT	-15.3	1661	0.003
24c	-2.0	-18.8	535	0.116
24d	Back PT	-56.8	3953	0.000
25c	-7.9	-8.9	517	0.137
25d	7.4	-4.4	864	0.004
26c	21.2 (12.3) <sup>c</sup>	13.4 ( <sup>d</sup> )	518	0.155
26d	Back PT	-7.5 ( <sup>d</sup> )	1911	0.001
27c	19.6 (12.0) <sup>c</sup>	−0.1 (8.1) <sup>c</sup>	590	0.136
27d	Back PT	-46.9 (°)	5545	0.001
28c	20.2 (15.2) <sup>c</sup>	-4.8 (5.9) <sup>c</sup>	1033	0.010
28d	25.3 (20.9) <sup>c</sup>	Back PT	_	_

<sup>a</sup>The Gibbs energies were calculated relative to the most stable HB complex of  ${\bf a}$  or  ${\bf b}$ -type.

<sup>b</sup>For the numeration of the guanidine nitrogen atoms see Figure 1. Attempts to obtain the N2 hydrogen-bonded structures resulted in the migration of the phenol to N1'.

 $^{c}\Delta G_{rel}$  for **26c–28d** were calculated using the corresponding **23c–25d** structure as the reference; the values calculated for non-stacked (HB) conformations **26a–28b** are given in parentheses.

<sup>d</sup>Converged to the stacked structure.

**26a-d-28a-d** than those obtained for their N1 analogues **22a-d-24a-d**. Therefore, the N1 atom is recognized as the preferred coordination site in comparison to the N2 position.

In the S<sub>1</sub> state, the lowest energy stacked conformations are generally preferred over the non-stacked ones.  $\pi$ -complexes show two minima corresponding to the neutral **c** and zwitterionic **d** structures irrespectively of the phenol (Table 3 and Figure 8), while the optimization of the complexes of the **b**-type usually ends in the stacked structure (Table S6). In particular, **d**-type structures were found to be lower in energy in the complexes with phenol **P1** and **P2**. In the case of **c**-type minima, relative stabilities vary depending on the complex. For example,  $\Delta G_{\rm rel}$  calculated for  $\pi$ -complexes of **1** with phenols **P1** or **P2** (**20c** and **21c**) are higher in energy than the HB ones (**20a** and **21a**) by 10.7 and 6.1 kJ mol<sup>-1</sup>, respectively. In the case of guanidine 2<sub>N1</sub>,  $\Delta G_{\rm rel}$  for the stacked complexes **23c** and **24c** amounts to 0.4 and

 $-18.8 \text{ kJ mol}^{-1}$ , respectively, indicating similar or higher stability of the stacked structures. For phenol **P3**, both stacked structures are more stable than the non-stacked but in contrast to **P1** and **P2**, internal proton transfer from phenol to guanidine is not favored ( $\Delta\Delta G_{rel}(25d-25c) = 4.5 \text{ kJ mol}^{-1}$ ). In other words, the PT process in the GS is highly unlikely even if the most acidic phenol **P3** is involved. However, changes in the acid/base properties of the components upon excitation make this process thermodynamically favorable for **P1** and especially for **P2** but not for **P3**.

For the optimized minima of the  $\pi$  stacked complexes (**c** and **d** type), we have calculated the lowest emission energy  $\lambda_{\rm Em}$  (Table 3). The results indicate a strong bathochromic shift and a decrease in the oscillator strength upon proton transfer. Analysis of the first five states in the complexes reveals the change in the character of the S<sub>1</sub> state on going from neutral **c**-type to zwitterionic **d**-type, from the local excitation (LE) at SBF to the charge transfer (CT) of the D-A type. In the **d** structures, the bright LE state became one of the higher energy states (S<sub>2</sub> to S<sub>4</sub> states, depending on the guanidine phenol pair). The calculations predict that  $\lambda_{\rm Em}$  from the LE state is estimated between 400 and 500 nm being comparable to those calculated for the uncomplexed protonated guanidine-SBFs.

## 4 | Conclusions

In this work, the results of the modeling novel single benzene fluorophores equipped with the guanidine subunit as the strongly basic group are presented. The employed calculations predict a weak decrease in the basicity upon excitation with  $\Delta G_{\rm p}$  values significantly higher than for the amino-SBFs. This implies a strong tendency of the guanidine-SBFs to be easily protonated in the  $S_1$  state if a proper photoacid is used. The protonated guanidines-SBFs show two minima in the S<sub>1</sub> state associated with ESIPT to the ester group with markedly different predicted emission wavelengths  $(\lambda_{Em})$ . In the case of **1** and **2**<sub>N2</sub>, the minima are almost isoenergetic which indicates the possibility of parallel existence of both forms and formation of the dual-emissive system. In neutral guanidine-SBFs, Stokes shift slightly smaller than in amines is predicted. The protonation induces a blue shift of the calculated  $\lambda_{\rm Em}$  relative to the neutrals unless ESIPT takes place. In the latter case, the change in the character of the S<sub>1</sub> state led to the  $\lambda_{\rm Em}$  shift toward the NIR region with a slight decrease in the oscillator strength.

Calculated aromaticity indices (both electronic MCI and magnetic NICS(1)<sub>zz</sub>) suggest strong antiaromaticity of both protonated and neutral forms in the FC region of the S<sub>1</sub> state which is alleviated to some extent by geometrical relaxation and especially by the ESIPT process in protonated structures. A comparison with the basicity data does not imply a significant impact of the change in the (anti)aromaticity upon ESIPT on the relative stability of two protonated forms. Also, the change in the antiaromaticity is similar for the neutral and the protonated guanidine-SBFs indicating that the guanidine subunit has minimal effect on the  $\pi$ -electronic density of the benzene ring.

The high basicity of the guanidine-SBFs in the S<sub>1</sub> state is suitable for the construction of the donor-acceptor complexes with phenols where spontaneous proton transfer is expected in the S<sub>1</sub> but not in the S<sub>0</sub> state. The calculations predicted  $\pi$ -complexes

as the most stable structures in the  $S_1$  state and that the excited state proton transfer is thermodynamically favored for phenol and its 4-OMe substituted derivative. Besides that, this excited state proton transfer process induces stabilization of several CT states characterized by the  $\pi(phenol) \rightarrow \pi^*(SBF)$  transition with very low oscillator strengths, destabilization of the ground state, and most likely loss of the fluorescence activity upon complexation.

The presented results indicate guanidine-SBFs as good systems for investigating the role of protonation on the photophysical properties of the SBFs under a much wider pH range than for ordinary amine-SBFs and also, they are promising core structures for constructing either on–off photoswitches or dual band emitting systems.

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#### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### References

1. B. Huang, M. Bates, and X. Zhuang, "Super-Resolution Fluorescence Microscopy," *Annual Review of Biochemistry* 78 (2009): 993–1016.

2. D. Wöll and C. Flors, "Super-Resolution Fluorescence Imaging for Materials Science," *Small Methods* 1 (2017): 1700191.

3. H. Kim, Y. Kim, and D. Lee, "Small Is Beautiful: Electronic Origin and Synthetic Evolution of Single-Benzene Fluorophores," *Accounts of Chemical Research* 57 (2024): 140–152.

4. Z. Liu, Y. Liu, F. Qi, H. Yan, Z. Jiang, and Y. Chen, "Flexible  $\pi$ -Conjugated 2,5-Diarylamino-Terephthalates: A New Class of Mechanochromic Luminophores With Tunable Aggregation States," *Chemistry—A European Journal* 26 (2020): 14963–14968.

5. N. Schröder, M. Schmidtmann, and J. Christoffers, "Diaminoterephthalate-EDTA and -EGTA Conjugates—"Turn on" Fluorescence Sensors for Zinc Ions," *European Journal of Organic Chemistry* 2021 (2021): 4260–4268.

6. N. Wache, C. Schröder, K.-W. Koch, and J. Christoffers, "Diaminoterephthalate Turn-on Fluorescence Probes for Thiols—Tagging of Recoverin and Tracking of Its Conformational Change," *ChemBioChem* 13 (2012): 993–998.

7. J. H. Jin, J. M. An, D. Kim, S. Lee, M. Kim, and D. Kim, "Amino-SBBF (Single Benzene-Based Fluorophore) Library: Its Synthesis, Photophysical Property, and Cellular Imaging Application," *Dyes and Pigments* 221 (2024): 111811.

8. Y. Kim, J. H. Oh, and D. Kim, "Recent Advances in Single-Benzene-Based Fluorophores: Physicochemical Properties and Applications," *Organic & Biomolecular Chemistry* 19, no. 5 (2021): 933–946, https://doi. org/10.1039/D0OB02387F. 9. R. Huang, B. Tang, K. Ye, C. Wang, and H. Zhang, "Flexible Luminescent Organic Bulk Crystal: 2D Elasticity Toward 3D Optical Waveguide," *Advanced Optical Materials* 7 (2019): 1900927.

10. R. Huang, Q. Qiao, T. Shen, et al., "Precision Molecular Engineering of Miniaturized Near-Infrared Fluorophores," *ChemRxiv* (2024): 1–18.

11. M. Ptaszek, *Progress in Molecular Biology and Translational Science: Chapter 3*, vol. 113, ed. M. C. Morris (Cambridge: Academic Press, 2013), 59–108.

12. F. de Moliner, F. Nadal-Bufi, and M. Vendrell, "Recent Advances in Minimal Fluorescent Probes for Optical Imaging," *Current Opinion in Chemical Biology* 80 (2024): 102458, https://doi.org/10.1016/j.cbpa. 2024.102458.

13. H. Kauffmann and L. Weissel, "Die Fluorescenz in Der Terephthalsäurereihe," *Justus Liebigs Annalen der Chemie* 393 (1912): 1–29.

14. Z. Bao, Y. Yang, X. Wu, et al., "Single-Benzene Fluorophores: Controlling Electron Density on Amino of 2,5-Diaminoterephthalates to Manipulate Optical/Electronic Properties for Efficient and Diversified Functions," *Advanced Functional Materials* 34 (2024): 2403954.

15. M. Rosenberg, C. Dahlstrand, K. Kilså, and H. Ottosson, "Excited State Aromaticity and Antiaromaticity: Opportunities for Photophysical and Photochemical Rationalizations," *Chemical Reviews* 114 (2014): 5379–5425.

16. H. Kim, W. Park, Y. Kim, M. Filatov, C. H. Choi, and D. Lee, "Relief of Excited-State Antiaromaticity Enables the Smallest Red Emitter," *Nature Communications* 12 (2021): 5409.

17. J. Yan, T. Slanina, J. Bergman, and H. Ottosson, "Photochemistry Driven by Excited-State Aromaticity Gain or Antiaromaticity Relief," *Chemistry—A European Journal* 29 (2023): e202203748.

18. M. Filatov, V. Mironov, and E. Kraka, "Unraveling the Effect of Aromaticity for the Dynamics of Excited States of Single Benzene Fluorophores," *Journal of Computational Chemistry* 45 (2024): 1033–1045.

19. P. J. Pacheco-Liñán, C. Alonso-Moreno, F. Carrillo-Hermosilla, et al., "Novel Fluorescence Guanidine Molecules for Selective Sulfate Anion Detection in Water Complex Samples Over a Wide pH Range," *ACS Sensors* 6 (2021): 3224–3233.

20. Z. Glasovac, L. Barešić, I. Antol, and D. Margetić, "Benzoylguanidines as Anion-Responsive Systems," *ChemPlusChem* 83 (2018): 845–854.

21. I. Antol, Z. Glasovac, D. Margetić, R. Crespo-Otero, and M. Barbatti, "Insights on the Auxochromic Properties of the Guanidinium Group," *Journal of Physical Chemistry*. A 120 (2016): 7088–7100.

22. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 16, Revision C.02* (Wallingford, CT: Gaussian, Inc, 2019).

23. Y. Zhao and D. G. Truhlar, "The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals," *Theoretical Chemistry Accounts* 120 (2008): 215–241.

24. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, "Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions," *Journal of Physical Chemistry*. B 113 (2009): 6378–6396.

25. C. Adamo and V. Barone, "Toward Reliable Density Functional Methods Without Adjustable Parameters: The PBE0 Model," *Journal of Chemical Physics* 110, no. 13 (1999): 6158–6169, https://doi.org/10.1063/1.478522.

26. T. Yanai, D. Tew, and N. Handy, "A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP)," *Chemical Physics Letters* 393, no. 1-3 (2004): 51–57, https://doi. org/10.1016/j.cplett.2004.06.011.

27. K. Aidas, C. Angeli, K. L. Bak, et al., "The Dalton Quantum Chemistry Program System," *WIREs Computational Molecular Science* 4 (2014): 269–284. 28. "Dalton, A Molecular Electronic Structure Program," Release v2020.1, 2022, http://daltonprogram.org.

29. M. Giambiagi, M. S. de Giambiagi, C. D. dos Santos Silva, and A. P. de Figueiredo, "Multicenter Bond Indices as a Measure of Aromaticity," *Physical Chemistry Chemical Physics* 2 (2000): 3381–3392.

30. E. Matito, M. Duran, and M. Solà, "The Aromatic Fluctuation Index (FLU): A New Aromaticity Index Based on Electron Delocalization," *Journal of Chemical Physics* 122, no. 1 (2005): 014109, https://doi.org/10.1063/1.1824895.

31. E. Matito, "An Electronic Aromaticity Index for Large Rings," *Physical Chemistry Chemical Physics* 18 (2016): 11839–11846.

32. T. Lu and F. Chen, "Multiwfn: A Multifunctional Wavefunction Analyzer," *Journal of Computational Chemistry* 33 (2012): 580–592.

33. H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, and P. v. R. Schleyer, "Which NICS Aromaticity Index for Planar  $\pi$  Rings Is Best?," *Organic Letters* 8, no. 5 (2008): 863–866, https://doi.org/10.1021/ol0529546.

34. G. Schaftenaar, E. Vlieg, and G. Vriend, "Molden 2.0: Quantum Chemistry Meets Proteins," *Journal of Computer-Aided Molecular Design* 31 (2017): 789–800.

35. G. Schaftenaar and J. H. Noordik, "Molden: A Pre- and Post-Processing Program for Molecular and Electronic Structures," *Journal* of Computer-Aided Molecular Design 14 (2000): 123–134.

36. A. E. Reed, L. A. Curtiss, and F. Weinhold, "Intermolecular Interactions From a Natural Bond Orbital, Donor-Acceptor Viewpoint," *Chemical Reviews* 88 (1988): 899–926.

37. M. Shimizu, Y. Takeda, M. Higashi, and T. Hiyama, "1,4-Bis(Alkeny l)-2,5-Dipiperidinobenzenes: Minimal Fluorophores Exhibiting Highly Efficient Emission in the Solid State," *Angewandte Chemie, International Edition* 48 (2009): 3653–3656.

38. M. J. G. Peach, P. Benfield, T. Helgaker, and D. J. Tozer, "Excitation Energies in Density Functional Theory: An Evaluation and a Diagnostic Test," *Journal of Chemical Physics* 128 (2008): 044118.

39. D. Hait, T. Zhu, D. P. McMahon, and T. Van Voorhis, "Prediction of Excited-State Energies and Singlet–Triplet Gaps of Charge-Transfer States Using a Restricted Open-Shell Kohn–Sham Approach," *Journal of Chemical Theory and Computation* 12 (2016): 3353–3359.

40. B. Tang, C. Wang, Y. Wang, and H. Zhang, "Efficient Red-Emissive Organic Crystals With Amplified Spontaneous Emissions Based on a Single Benzene Framework," *Angewandte Chemie, International Edition* 56 (2017): 12543–12547.

41. R. Zhou, Y. Cui, J. Dai, et al., "A Red-Emissive Fluorescent Probe With a Compact Single-Benzene-Based Skeleton for Cell Imaging of Lipid Droplets," *Advanced Optical Materials* 8 (2020): 1902123.

42. J. M. Leal and B. Garcia, "Effects of Substituents on UV Spectra of Aniline and Anilinium Ion Derivatives. Hammett Correlations," *Zeitschrift fur Physikalische Chemie (Leipzig)* 269, no. 1 (1988): 26–32, https://doi.org/10.1515/zpch-1988-26906.

43. H. Liu, S. Zhang, L. Ding, and Y. Fang, "Dual-State Efficient Chromophore With pH-Responsive and Solvatofluorochromic Properties Based on an Asymmetric Single Benzene Framework," *Chemical Communications* 57 (2021): 4011–4014.

44. Y. Kim, H. Kim, J. B. Son, et al., "Single-Benzene Dual-Emitters Harness Excited-State Antiaromaticity for White Light Generation and Fluorescence Imaging," *Angewandte Chemie, International Edition* 62 (2023): e202302107.

45. K. Tsutsumi and H. Shizuka, "Excited State pK\*a Values of Naphthylamines: Proton-Induced Fluorescence Quenching," *Chemical Physics Letters* 52 (1977): 485–488.

46. Z. Wen, L. J. Karas, C.-H. Wu, and J. I. Wu, "How Does Excited-State Antiaromaticity Affect the Acidity Strengths of Photoacids?," *Chemical*  Communications 56, no. 60 (2020): 8380-8383, https://doi.org/10.1039/ D0CC02952A.

47. S. Tajima, S. Shiobara, H. Shizuka, and S. Tobita, "Excited-State Proton-Dissociation of N-Alkylated Anilinium Ions in Aqueous Solution Studied by Picosecond Fluorescence Measurements," *Physical Chemistry Chemical Physics* 4 (2002): 3376–3382.

48. J. Draženović, C. J. Laconsay, N. Došlić, J. I. Wu, and N. Basarić, "Excited-State Antiaromaticity Relief Drives Facile Photoprotonation of Carbons in Aminobiphenyls," *Chemical Science* 15 (2024): 5225–5237.

49. E. D. Raczyńska, M. K. Cyrański, M. Gutowski, et al., "Consequences of Proton Transfer in Guanidine," *Journal of Physical Organic Chemistry* 16 (2003): 91–106.

50. F. Feixas, E. Matito, J. Poater, and M. Solà, "On the Performance of Some Aromaticity Indices: A Critical Assessment Using a Test Set," *Journal of Computational Chemistry* 29 (2008): 1543–1554.

51. C. Foroutan-Nejad, "Magnetic Antiaromaticity–Paratropicity–Does Not Necessarily Imply Instability," *Journal of Organic Chemistry* 88 (2023): 14831–14835.

52. P. Preethalayam, N. Proos Vedin, S. Radenković, and H. Ottosson, "Azaboracyclooctatetraenes Reveal That the Different Aspects of Triplet State Baird-Aromaticity Are Nothing but Different," *Journal of Physical Organic Chemistry* 36 (2023): e4455.

53. Y.-C. Lin, D. Sundholm, and J. Jusélius, "On the Aromaticity of the Planar Hydrogen-Bonded (HF)3Trimer," *Journal of Chemical Theory and Computation* 2 (2006): 761–764.

54. D. Xing, F. Glöcklhofer, and F. Plasser, "Proton Transfer Induced Excited-State Aromaticity Gain for Chromophores With Maximal Stokes Shifts," *Chemical Science* 15 (2024): 17918–17926.

55. V. Balzani, P. Ceroni, and A. Juris, *Photochemistry and Photophysics. Concepts, Research, Applications* (Weinheim, Germany: Wiley-VCH Verlag, 2014), 117–120.

56. B. Bartolomei, G. Gentile, C. Rosso, G. Filippini, and M. Prato, "Turning the Light on Phenols: New Opportunities in Organic Synthesis," *Chemistry—A European Journal* 27 (2021): 16062–16070.

57. A. Olasz, P. Mignon, F. De Proft, T. Veszprémi, and P. Geerlings, "Effect of the  $\pi$ - $\pi$  Stacking Interaction on the Acidity of Phenol," *Chemical Physics Letters* 407 (2005): 504–509.

58. T. Hossen and K. Sahu, "Photo-Induced Electron Transfer or Proton-Coupled Electron Transfer in Methylbipyridine/Phenol Complexes: A Time-Dependent Density Functional Theory Investigation," *Journal of Physical Chemistry. A* 123 (2019): 8122–8129.

#### **Supporting Information**

Additional supporting information can be found online in the Supporting Information section.