**HYDROXYAROMATIC FLUOROPHORES**

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1. Introduction to Table S1

For each compound, four structures were optimized: the $S_0$ and $S_1$ states of both neutral and anion forms. The $S_0$ structures were optimized using aug-cc-pVDZ or def2-SVPD basis set except in one case (pyranine) where def2-TZVP basis set was used. For both neutral and anion in each pair, the same functional and basis set were used to ensure comparability of the properties in the ground states. For the excited states ($S_1$), most of the structures are optimized using B3LYP functional and def2-SVPD basis set. If an optimization failed to converge to a minimum, the basis set was changed to aug-cc-pVDZ. In a few cases, others basis sets (e.g., def2-SV(P) and def2-TZVP) were used in order to obtain a true minimum (as characterized by all positive vibrational frequencies from the Hessian matrix). For several species for which calculations with B3LYP functional were not able to converge to a minimum on the $S_1$ state, LC-BLYP functional was used. For neutral HP-TZ1 and HP-TZ2, calculations with def2-SVPD were not able to converge to the minima, and 6-311G* basis set was instead used.

2. Table S1. Methods and basis sets used in the geometry optimizations.

|        | Ground state (neutral) | Excited state (neutral) | Ground state (anion) | Excited State (anion) |
|--------|------------------------|-------------------------|----------------------|-----------------------|
|        | Method | Basis* | Method | Basis | Method | Basis* | Method | Basis |
| (1)    | xanthene | B3LYP | aug-cc-pVDZ | B3LYP | aug-cc-pVDZ | B3LYP | aug-cc-pVDZ | B3LYP | def2-SV(P) |
| (2)    | p-HBDI | B3LYP | aug-cc-pVDZ | B3LYP | def2-TZVP | B3LYP | aug-cc-pVDZ | B3LYP | def2-SVPD |
| (3)    | 7HC | B3LYP | aug-cc-pVDZ | B3LYP | def2-SV(P) | B3LYP | aug-cc-pVDZ | B3LYP | def2-SVPD |
| (4)    | 2-naphthol | B3LYP | aug-cc-pVDZ | B3LYP | aug-cc-pVDZ | B3LYP | aug-cc-pVDZ | B3LYP | def2-SVPD |
| (5)    | pyranine | B3LYP | def2-TZVP | B3LYP | def2-TZVP | B3LYP | def2-TZVP | B3LYP | def2-TZVP |
| (6)    | HBO (N) | B3LYP | aug-cc-pVDZ | B3LYP | def2-SVPD | B3LYP | aug-cc-pVDZ | LC-BLYP | def2-SVPD |
| (6')   | HBO (T) | - | - | B3LYP | def2-SVPD | - | - | - | - |
| (7)    | BIPYVHBO (N) | B3LYP | aug-cc-pVDZ | B3LYP | def2-SVPD | B3LYP | aug-cc-pVDZ | B3LYP | def2-SVPD |
| (7')   | BIPYVHBO (T) | - | - | B3LYP | def2-SVPD | - | - | - | - |
| (8)    | HP-TZ1 | B3LYP | def2-SVPD | LC-BLYP | 6-311G* | B3LYP | def2-SVPD | LC-BLYP | def2-SVPD |
| (9)    | HP-TZ2 | B3LYP | def2-SVPD | LC-BLYP | 6-311G* | B3LYP | def2-SVPD | LC-BLYP | def2-SVPD |
| (10)   | HP-TZ3 | B3LYP | aug-cc-pVDZ | - | - | B3LYP | aug-cc-pVDZ | LC-BLYP | def2-SVPD |

a. The basis sets for the ground state optimizations of the neutral and anion of the same compound were kept the same, so that some properties of the neutral and anion forms are comparable.
3. **Table S2.** Calculated excitation energies (S₀ to S₁) at relaxed S₀ geometries (aug-cc-pVDZ basis set).²

| Entry | Name     | \( \lambda \) (N)/nm (exp/nm) | f (N) | Sol. | \( \Delta E \) (N)/eV | \( \lambda \) (A)/nm (exp/nm) | f (A) | Sol. | \( \Delta E \) (A)/eV |
|-------|----------|-------------------------------|------|------|------------------|-------------------------------|------|------|------------------|
| 1     | xanthene | 422 (508)                     | 0.67 | EtOH | 0.50             | 510 (508)                     | 0.89 | EtOH | -0.01            |
| 2     | p-HBDI   | 365 (395)                     | 0.69 | water| 0.26             | 474 (475)                     | 0.98 | water| 0.01             |
| 3     | 7HC      | 303 (324)                     | 0.42 | water| 0.27             | 393 (366)                     | 0.54 | water| -0.23            |
| 4     | 2-naphthol | 297 (329)                  | 0.05 | water| 0.41             | 378 (350)                     | 0.11 | water| -0.26            |
| 5     | pyranine | 395 (400)                     | 0.58 | water| 0.04             | 538 (450)                     | 0.54 | water| -0.45            |
| 6     | HBO      | 306 (333)                     | 0.53 | DMSO | 0.33             | 401 (400)                     | 0.49 | DMSO | -0.01            |
| 7     | BIPYVHBOP | 345 (350)                  | 1.19 | DMSO | 0.05             | 449 (457)                     | 1.48 | DMSO | 0.05             |
| 8     | HP-TZ1   | 303e (299)                    | 0.74d| ACN  | -0.05            | 350 (335)                     | 0.32 | ACN  | -0.16            |
| 9     | HP-TZ2   | 323 (318)                     | 0.77 | DMSO | -0.06            | 346 (353)                     | 0.36 | DMSO | 0.07             |
| 10    | HP-TZ3   | 289 (295)                     | 0.50 | DMSO | 0.06             | 356 (361)                     | 0.31 | DMSO | 0.05             |

a. N = neutral; A = anion, i.e., conjugate base; \( \Delta E = E (\lambda_{(\text{GS})}, \text{calculated}) – E (\lambda_{(\text{abs, max})}, \text{experimental}) \), in eV. The experimental data are taken from Table 1. The neutral and anion of each compound were optimized using DFT/B3LYP and the same basis sets (Table S1). Aug-cc-pVDZ basis sets were used for the single point calculations to acquire the excitation energy values in this Table. The excitation energies using def2-SVPD basis sets are included in Table S3; b. The mean absolute deviations of \( \Delta E \) (N) and \( \Delta E \) (A) is 0.20 and 0.13 eV, respectively; c. Overestimated energies are marked blue, while underestimated energies are marked red; d. excitation energy of S₂ instead of S₁. The latter has a much smaller oscillator strength that would have been obscured in the experimental absorption spectrum.
4. **Table S3.** Calculated excitation energies (S₀ → S₁) at relaxed S₀ geometries (def2-SVPD basis set).\(^a,b\)

| Entry | Name       | \(\lambda\) (N)/nm (exp/nm) | f (N) | Sol. | \(\Delta E\) (N)/eV\(^c\) | \(\lambda\) (A)/nm (exp/nm) | f (A) | Sol. | \(\Delta E\) (A)/eV\(^c\) |
|-------|------------|------------------------------|-------|------|-----------------------------|-----------------------------|-------|------|-----------------------------|
| 1     | xanthene   | 420 (508)                    | 0.68  | EtOH | 0.51                        | 511 (508)                   | 0.89  | EtOH | -0.01                        |
| 2     | p-HBDI     | 361 (395)                    | 0.71  | water| 0.30                        | 475 (475)                   | 0.98  | water| 0                           |
| 3     | 7HC        | 301 (324)                    | 0.42  | water| 0.29                        | 393 (366)                   | 0.55  | water| -0.23                        |
| 4     | 2-naphthol | 294 (329)                    | 0.04  | water| 0.45                        | 372 (350)                   | 0.11  | water| -0.21                        |
| 5     | pyranine   | 392 (400)                    | 0.58  | water| 0.06                        | 536 (450)                   | 0.55  | water| -0.44                        |
| 6     | HBO        | 304 (333)                    | 0.50  | DMSO | 0.36                        | 398 (400)                   | 0.48  | DMSO | 0.02                         |
| 7     | BIPYVHBO   | 338 (350)                    | 1.07  | DMSO | 0.13                        | 442 (457)                   | 1.50  | DMSO | 0.09                         |
| 8     | HP-TZ1     | 297\(^d\) (299)             | 0.78\(^d\) | DMSO | 0.02                        | 343 (335)                   | 0.33  | ACN  | -0.09                        |
| 9     | HP-TZ2     | 312 (318)                    | 0.82  | DMSO | 0.07                        | 340 (353)                   | 0.36  | DMSO | 0.13                         |
| 10    | HP-TZ3     | 286 (293)                    | 0.46  | DCM  | 0.10                        | 351 (361)                   | 0.31  | DMSO | 0.10                         |

\(^a\) N = neutral; A = anion, i.e., conjugate base; \(\Delta E = E(\lambda_{GS}\text{, calculated}) - E(\lambda_{\text{abs. max}},\text{ experimental})\), in eV. The experimental data are taken from Table 1. Def2-SVPD basis sets were used for acquiring the data in this Table. The excitation energies using aug-cc-pVDZ basis sets are included in Table S2; \(^b\) The mean absolute deviations of \(\Delta E\) (N) and \(\Delta E\) (A) is 0.23 and 0.13 eV, respectively; \(^c\) Overestimated energies are marked blue, while underestimated energies are marked red; \(^d\) Excitation energy of S₂ instead of S₁. The latter has a much smaller oscillator strength that would have been obscured in the experimental absorption spectrum.
5. Table S4. Calculated excitation energies ($S_0 \rightarrow S_1$) at relaxed $S_1$ geometries (aug-cc-pVDZ basis set).\textsuperscript{a,b}

| Entry | Name | $\lambda (N^*)$/nm (exp/nm) | $f (N^*)$ | Sol. | $\Delta E (N^*)$/eV\textsuperscript{c} | $\lambda (A^*)$/nm (exp/nm) | $f (A^*)$ | Sol. | $\Delta E (A^*)$/eV\textsuperscript{c} |
|-------|------|--------------------------|--------|-----|-----------------------------|--------------------------|--------|-----|-----------------------------|
| 1     | xanthene | 556 (517) | 0.49 | EtOH | -0.17 | 608 (517) | 0.64 | EtOH | -0.36 |
| 2     | $p$-HBDI | 443 (460) | 0.66 | water | 0.10 | 575 (508) | 0.70 | water | -0.28 |
| 3     | 7HC | 428 (397) | 0.19 | MeOH | -0.23 | 516 (453) | 0.32 | water | -0.33 |
| 4     | 2-naphthol | 333 (360) | 0.08 | water | 0.28 | 429 (425) | 0.10 | water | -0.03 |
| 5     | pyranine | 450 (418) | 0.65 | EtOH | -0.21 | 575 (510) | 0.51 | water | -0.27 |
| 6     | HBO (N) | 365 (370) | 0.39 | DMSO | 0.05 | 460 (450) | 0.41 | DMSO | -0.06 |
| 6’    | HBO (T) | 514 (480) | 0.23 | DCM | -0.17 | - | - | - |
| 7     | BIPYVHBO (N) | 447 (445) | 0.13 | DMSO | -0.01 | 782 (585) | 0.63 | DMSO | -0.53 |
| 7’    | BIPYVHBO (T) | 538 (550) | 0.38 | DCM | 0.05 | - | - | - |
| 8     | HP-TZ1 | 499 (449) | 0.18 | DCM | -0.28 | 429 (434) | 0.32 | ACN | 0.03 |
| 9     | HP-TZ2 | 451 (409) | 0.61 | DCM | -0.28 | 660 (524) | 0.05 | DMSO | -0.49 |
| 10    | HP-TZ3 | - | - | - | - | 455 (435) | 0.31 | DMSO | -0.13 |

a. N = neutral; A = anion, i.e., conjugate base; $\Delta E = E (\lambda_{(i @ xS_j)}$, calculated) $- E (\lambda_{(em, max)}$, experimental), in eV. The experimental data were taken from Table 1. Aug-cc-pVDZ basis sets were used for acquiring the data in this Table. The excitation energies using def2-SVPD basis sets are included in Table S5; b. The mean absolute deviations of $\Delta E (N^*)$ and $\Delta E (A^*)$ is 0.17 and 0.25 eV, respectively; c. Overestimated energies are marked blue, while underestimated energies are marked red; d. *: excited state.
### 6. Table S5. Calculated excitation energies ($S_0 \rightarrow S_1$) at relaxed $S_1$ geometries (def2-SVPD basis set)\(^{a,b}\)

| Entry | Name     | $\lambda (N^*)$/nm (exp/nm) | $f (N^*)$ | Sol. | $\Delta E (N^*)$/eV\(^c\) | $\lambda (A^*)$/nm (exp/nm) | $f (A^*)$ | Sol. | $\Delta E (A^*)$/eV\(^c\) |
|-------|----------|-----------------------------|-----------|------|-----------------------------|-----------------------------|-----------|------|-----------------------------|
| 1     | xanthene | 556 (517)                   | 0.49      | EtOH | -0.17                       | 611 (517)                   | 0.64      | EtOH | -0.37                       |
| 2     | p-HBDI   | 439 (460)                   | 0.69      | water| 0.13                        | 521 (508)                   | 0.90      | water| -0.06                       |
| 3     | 7HC      | 425 (397)                   | 0.19      | MeOH | -0.21                       | 517 (453)                   | 0.32      | water| -0.34                       |
| 4     | 2-naphthol | 329 (360)               | 0.07      | water| 0.32                        | 477 (425)                   | 0.07      | water| -0.32                       |
| 5     | pyranine | 447 (418)                   | 0.66      | EtOH | -0.19                       | 573 (510)                   | 0.52      | water| -0.27                       |
| 6     | HBO (N)  | 365 (370)                   | 0.37      | DMSO | 0.05                        | 458 (450)                   | 0.41      | DMSO | -0.05                       |
| 6'    | HBO (T)  | 516 (480)                   | 0.23      | DCM  | -0.18                       | -                           | -         | -   | -                           |
| 7     | BIPYVHBO (N) | 442 (445)             | 0.13      | DMSO | 0.02                        | 776 (585)                   | 0.63      | DMSO | -0.52                       |
| 7'    | BIPYVHBO (T) | 537 (550)              | 0.38      | DCM  | 0.05                        | -                           | -         | -   | -                           |
| 8     | HP-TZ1   | 490 (449)                   | 0.17      | DCM  | -0.23                       | 419 (434)                   | 0.33      | ACN  | 0.10                        |
| 9     | HP-TZ2   | 435 (409)                   | 0.67      | DCM  | -0.18                       | 643 (524)                   | 0.05      | DMSO | -0.44                       |
| 10    | HP-TZ3   | -                           | -         | -    | -                           | 448 (435)                   | 0.31      | DMSO | -0.08                       |

\(^{a}\) $N =$ neutral; $A =$ anion, i.e., conjugate base; $\Delta E = E (\lambda_{\text{em}, \text{max}}$ experimental) $- E (\lambda_{\text{em}, \text{max}}$ calculated), in eV. The experimental data were taken from Table 1. Def2-SVPD basis sets were used for acquiring the data in this Table. The excitation energies using aug-cc-pVDZ basis sets are included in Table S4; \(^{b}\) The mean absolute deviations of $\Delta E (N^*)$ and $\Delta E (A^*)$ is 0.16 and 0.26 eV, respectively; \(^{c}\) Overestimated energies are marked blue, while underestimated energies are marked red; \(^{d}\)*: excited state.
7. Table S6. Changes of frontier molecular orbitals (FMOs in eV) upon deprotonation at ground state (GS) geometries of compounds 1-7.\textsuperscript{a}

| Entry | Name   | Solvent | H to L contr. to S\textsubscript{1} (N, A)\textsuperscript{a} | \(\Delta\text{HOMO (GS)}/\text{eV}\textsuperscript{b} \) | \(\Delta\text{LUMO (GS)}/\text{eV}\textsuperscript{b} \) |
|-------|--------|---------|-------------------------------------------------|-----------------|-----------------|
| 1     | xanthene | EtOH    | 86%, 95%                                       | 1.1             | 0.6             |
| 2     | p-HBDI  | water   | 81%, 83%                                       | 1.2             | 0.3             |
| 3     | 7HC     | water   | 84%, 93%                                       | 1.4             | 0.4             |
| 4     | 2-naphthol | water   | 52%, 85%                                       | 1.3             | 0.4             |
| 5     | pyranine | water   | 90%, 95%                                       | 1.2             | 0.5             |
| 6     | HBO     | DMSO    | 63%, 85%                                       | 1.3             | 0.5             |
| 7     | BIPYVHBO | DMSO    | 81%, 79%                                       | 1.1             | 0.2             |

\(\Delta\text{HOMO} = \text{HOMO (A)} – \text{HOMO (N)}, \Delta\text{LUMO} = \text{LUMO (A)} – \text{LUMO (N)}.\)

\textsuperscript{a} N = neutral, A = anion; b. \(\Delta\text{HOMO} = \text{HOMO (A)} – \text{HOMO (N)}, \Delta\text{LUMO} = \text{LUMO (A)} – \text{LUMO (N)}.\)
8. The saga of optimizing the excited state of HBO anion

Both planar conformers of HBO anion (see Scheme 8 in the article) were identified as minima on the GS, between which the cis-planar is more stable than the trans-planar (Table S7). On the S1 surface (XS), only the twisted conformer was identified as a minimum (relaxed from both cis- and trans-planar initial structures), with an excitation energy (679 nm) far less than the experimental value and an almost non-existent oscillator strength (0.0002).

Table S7. Relative energies of three conformers of the HBO anion in ground state (GS), first excited state (XS), and second excited state (XXS) when optimized with (TD)DFT/B3LYP.a

|            | Trans-planar | Twisted | Cis-planar |
|------------|--------------|---------|------------|
| GS         | 2.5 kcal/mol | -       | 0          |
| XS         | -            | 0       | -          |
| XXS        | -4 kcal/molb | 0       | -4 kcal/molb |

a. The geometry of the XS of the cis-planar conformer was later successfully relaxed at TDDFT/LC-BLYP/def2-SVP level of theory; b. geometry minimization NOT converged, while S1 and S2 excitation energies are within only 1 nm (e.g., 484 and 485 nm) and flipping during the iterations.

The three conformers were also minimized on the S2 surface (XXS). Again, only the twisted conformer converged to a minimum. What is peculiar about the conformers on the S2 surface occurred when the cis- or trans-planar initial structures were minimized with the C1 symmetry. Both optimizations failed to converge but reached to lower excited state energies than the twisted minimum (Table S7). When examining the excitation energy data of each iteration, both the S1 and S2 excitation energies (~ 484 nm with oscillator strength of ~ 0.21) were becoming close to the experimental emission energy (~ 450 nm), and the energetic difference between S1 and S2 was reduced to vanishingly small values during the final stage of the unfinished minimization. The two excitation energy values (and oscillator strengths) were flipping between these two states. Therefore, one may interpret that the S1 and S2 surfaces are closing in at this very geometry to the extent that the minimization algorithm becomes unstable. The excitation energy and oscillator strength values recorded during the final stage of iterations of the unconverged, relatively planar structures on the S2 surface are consistent with the experimental emission wavelength and the quantum yield of the HBO anion, which led us to believe that a planar excited state on either S1 or S2 state produces the experimentally observed emission.

The inability to converge at an emissive excited state of HBO anion that would produce excitation energy comparable to the experimental emission wavelength prompted us to examine the appropriateness of the B3LYP functional. The excess charge of an anion may require the long-range part of the exchange to be treated by 100% HF in order to obtain accurate exchange potential outside the molecule. Using TDDFT/LC-BLYP, the optimization of the S1 state of the HBO anion converged to an emissive XS structure (judged by the oscillator strength) with an excitation energy comparable with the experimentally observed emission (Tables S4-S5). The success of the convergence is attributed to the
fact that the $S_1$ and $S_2$ states are now sufficiently separated using the LC-BLYP functional. The issues that were faced by the $S_1$ state of HBO anion reappeared with the optimizations of the $S_1$ states of HP-TZ1 and HP-TZ2 (both neutral and anion), and HP-TZ3 anion. These 5 structures were eventually optimized using TDDFT/LC-BLYP.

9. **Table S8.** Comparison of excitation energy values of 6 structures based on either TDDFT/CAM-B3LYP or TDDFT/LC-BLYP optimized geometries.\(^a\)

| Name          | $\lambda_{\text{em, exp}}$/nm (solvent) | $\lambda_{\text{calc}}$/nm (LC-BLYP) | $\lambda_{\text{calc}}$/nm (CAM-B3LYP) | $\Delta E$/eV | $\Delta E$/eV |
|---------------|----------------------------------------|--------------------------------------|----------------------------------------|----------------|----------------|
| HBO, anion    | 450 (DMSO)                             | 460                                  | 461                                    | 0.41           | -0.06          |
|               |                                        |                                      |                                        | 0.38           | -0.07          |
| HP-TZ1, neutral | 449 (DCM)                             | 499                                  | 509                                    | 0.18           | -0.28          |
|               |                                        |                                      |                                        | 0.17           | -0.33          |
| HP-TZ1, anion | 434 (ACN)                             | 429                                  | 477\(^b\)                             | 0.32           | 0.03           |
|               |                                        |                                      |                                        |                |                |
| HP-TZ2, neutral | 409 (DCM)                             | 451                                  | 467                                    | 0.61           | -0.28          |
|               |                                        |                                      |                                        | 0.59           | -0.38          |
| HP-TZ2, anion | 524 (DMSO)                             | 660                                  | 702                                    | 0.05           | -0.49          |
|               |                                        |                                      |                                        | 0.04           | -0.60          |
| HP-TZ3, anion | 435 (DMSO)                             | 455                                  | 457                                    | 0.31           | -0.13          |
|               |                                        |                                      |                                        | 0.30           | -0.14          |

\(^a\) The left side of the double line lists the calculated excitation energy, oscillator strength, and deviation from experimental value based on TDDFT/LC-BLYP optimized $S_1$ geometries (also listed in Tables S4 and S5), while the right side of the double line lists the values based on TDDFT/CAM-B3LYP optimized $S_1$ geometries. \(^b\) The single point excitation energy calculations on ADC(2)/PTED-COSMO level of theory did not converge. The data listed are those of the last iteration.