

Supporting Information:
Benchmarking Charge-Transfer Excited States in TADF Emitters:
 Δ DFT outperforms TD-DFT for Emission Energies

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All optimized geometries as well as input and output files for the calculations are provided separately as a .zip archive in the Supporting Information.

A. Computational Details

The Q-Chem 5.4 program package[1] was used for all quantum-chemical calculations. Foremost, we used PBE[2]-based hybrid functionals, namely, the global hybrids PBE0[3] and PBE38[4], and the optimally-tuned range-separated hybrids OT-LC- ω PBE [5] and OT-LRC- ω PBEh [6]. Additionally, we used the OT- ω B97M-V functional since it was the best performer on the original STGABS27 set.[7] The optimally-tuned range-separation parameters ω were taken from our previous work on the STGABS27 set.[7, 8] For all functionals not including non-local correlation, the DFT-D4[9, 10] dispersion correction was applied with the default damping parameter for the untuned functional.[11] All but exploratory calculations with the def2-TZVPP basis set concerning the basis set convergence use the def2-SVP basis set.[12, 13]

Measurement-specific dielectric constant (ϵ) and refractive index (n) were used in all solvent models. The dielectric constant for the host material CBP (4,4'-bis(carbazol-9-yl)biphenyl) was estimated at 3.5 since values of both 3.0 and 4.0 appear in the literature. A comparison of mCP ($\epsilon=2.84$) and CBP as a host material of donor-acceptor TADF emitters showed a larger bathochromic shift of the emission peak in CBP, which supports a dielectric constant value larger than 3.0.[14] If no experimental values were available for either quantity, we set $\epsilon = 3.0$ and $n^2 = 2.25$. The Q-Chem default values were used for all other parameters of the solvation model.

Due to their different response to the dielectric environment, the lowest charge-transfer (CT) state and lowest locally-excited (LE) state were considered for both emission energies and geometry optimization. However, the singlet state has a strong CT character in all but the MR-TADF emitters DABNA-1 and DABNA-2.

1. Time-dependent density functional theory

All TD-DFT calculations were performed in Tamm-Dancoff approximation (TDA-DFT).[15, 16] Solvation effects were generally treated with the iterative state-specific polarizable continuum model (SS-PCM[17–21], newly implemented in Q-Chem 6.1.0). Here, the initial excited state is treated in the equilibrium solvation regime dominated by the dielectric constant ϵ , while the final ground state reached after emission is treated in the non-equilibrium regime. For this, we calculate the ground state in the reaction field of the equilibrated excited state and employ a first-order perturbative ptSS-PCM correction to relax the fast electronic solvent degrees of freedom (DOFs) characterized by the refractive index ($\epsilon_\infty = n^2$). The solvation models always employ the relaxed excited state density, and all PCM treatments were performed in the integral-equation-formalism (IEF-PCM [22]). In exploratory calculations, we further employ the linear-response polarizable continuum model (LR-PCM [23]) as well as a combination of SS- and LR-PCM.

All calculations were performed at the geometries optimized with TDA-DFT using the same density functional as in the later calculation of the emission energies. However, the optimizations were performed without a solvent model due to the unavailability of analytical nuclear gradients for the iterative implementation of SS-PCM. Because of the impact of the dielectric environment on the state ordering for charge-transfer (CT) and locally-excited (LE) states, the geometry optimizations of singlet and triplet were started for the lowest states of each character. To optimize higher-lying excited states with TDA-based methods, state-following was used, as implemented in Q-Chem (based on the overlap density of the state before and after each optimization step). For some molecules, the geometry optimization converged to the same lowest state despite the state-following algorithm. Only the lowest optimized state was used in the later calculations.

2. States-specific Δ DFT

All Δ DFT calculations were carried out with a development version of the Q-Chem program package 5.4.2. For the SCF calculation of the UKS wavefunctions, the initial maximum-overlap-method (IMOM)[24, 25] was applied to prevent variational collapse to the ground state. The targeted excited-state transition for Δ UKS was modeled via the *\$occupied* block, where individual electrons can be promoted from occupied to virtual orbitals. A converged ground-state SCF calculation served as the initial SCF guess for both Δ UKS and Δ ROKS calculations. In some difficult cases, where excitation from multiple donors was possible, the converged SCF solution of the cationic species

was used instead. This helps to localize the charge-transfer excitation to a single donor-acceptor pair, which in all studied cases is significantly lower in energy than the corresponding charge-transfer states delocalized over two or more donor units. The SCF convergence was set to 10^{-8} for Δ UKS calculations and to 10^{-5} for Δ ROKS calculations (the ROKS error metric for convergence is the RMS gradient). In Δ UKS calculations, DIIS was used for SCF convergence acceleration, while DIIS was coupled with the geometric direct minimization (GDM[26]) converger for Δ ROKS. The integral-equation formalism of the polarizable continuum model (IEF-PCM) was applied for implicit solvation. For the geometry optimizations of some difficult cases, the maximum number of optimization cycles had to be increased to 250 for convergence. As input geometries, optimized geometries from a previous study[7] were used. The default settings were applied for all other keywords, e.g., the standard quadrature grids[27] were used.

B. Complete calculated emission energies

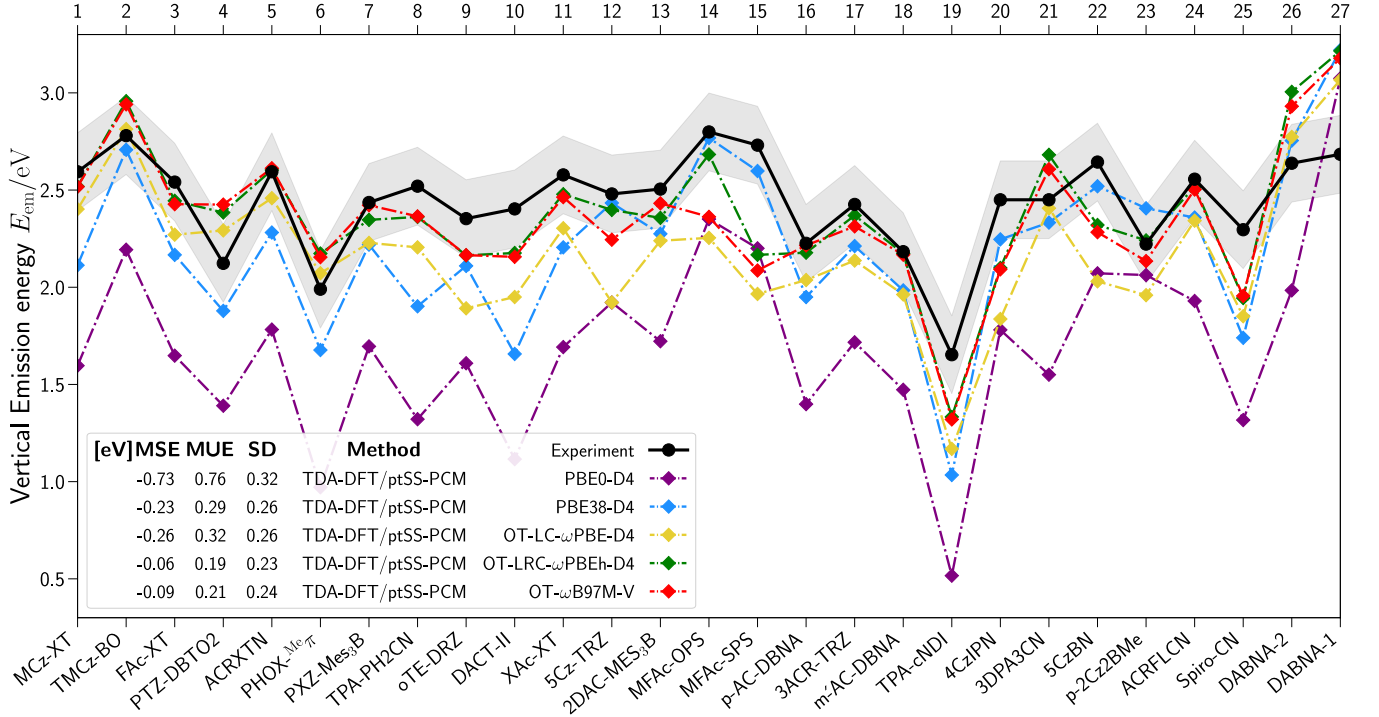


FIG. S1. Calculated emission energies E_{em} for different functionals with TDA-DFT/ptSS-PCM at the consistently optimized S_1 geometry. ϵ and n^2 were chosen for the measurement-specific solvent. An estimated uncertainty of ± 0.2 eV for the experimental reference (black) is marked by a gray band. MSE, MUE, and SD values for the set are tabulated.

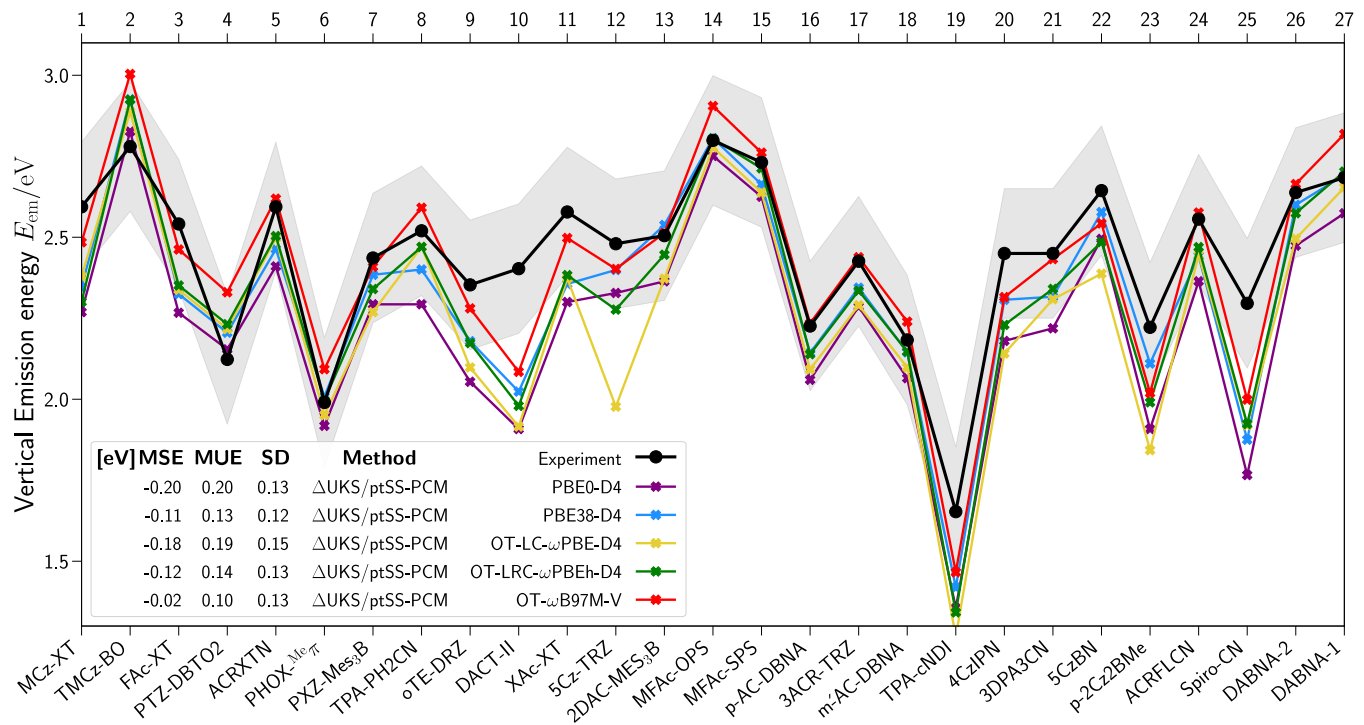


FIG. S2. Calculated emission energies E_{em} for different functionals with Δ UKS/ptSS-PCM at the consistently optimized S_1 geometry. ϵ and n^2 were chosen for the measurement-specific solvent. An estimated uncertainty of ± 0.2 eV for the experimental reference (black) is marked by a gray band. MSE, MUE, and SD values for the set are tabulated.

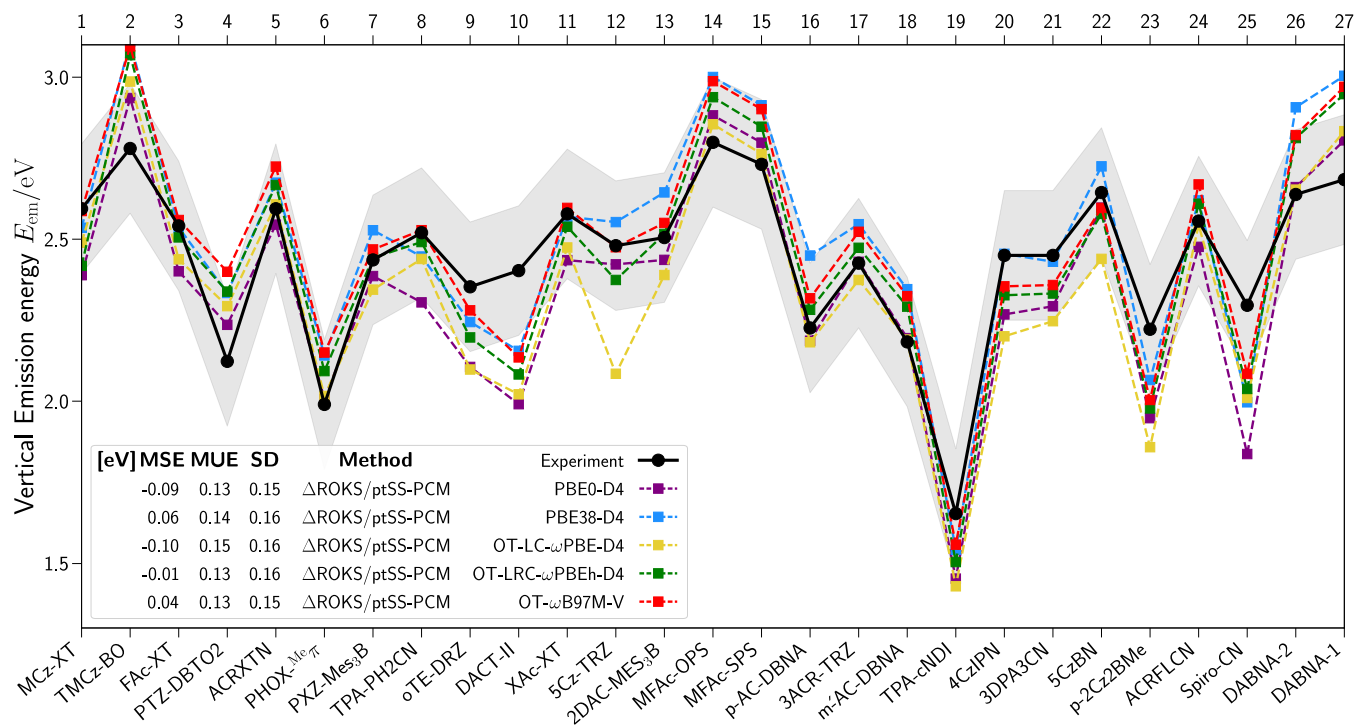


FIG. S3. Calculated emission energies E_{em} for different functionals with Δ ROKS/ptSS-PCM at the consistently optimized S_1 geometry. ϵ and n^2 were chosen for the measurement-specific solvent. An estimated uncertainty of ± 0.2 eV for the experimental reference (black) is marked by a gray band. MSE, MUE, and SD values for the set are tabulated.

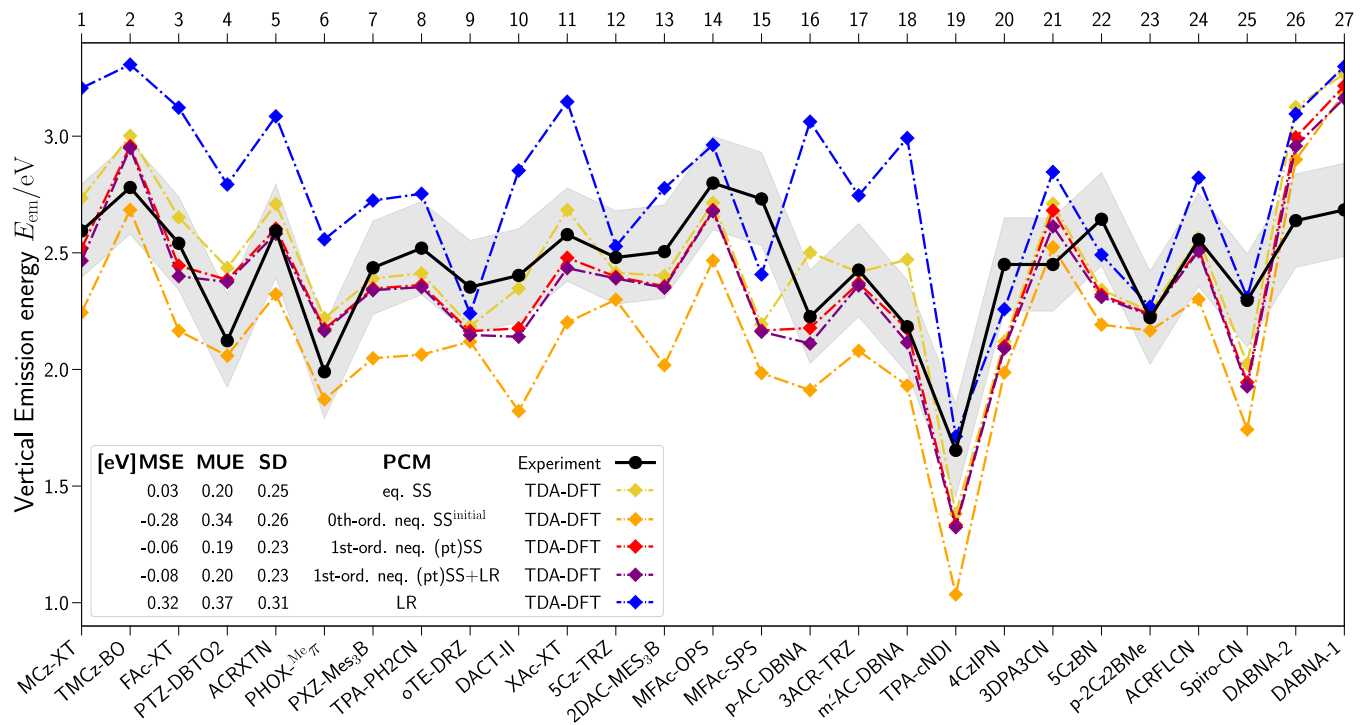


FIG. S4. Calculated emission energies E_{em} for different solvation models with TDA-DFT using the OT-LRC- ω PBEh-D4 functional (dash-dotted lines) at the consistently optimized S_1 geometry. ϵ and n^2 were chosen for the measurement-specific solvent. An estimated uncertainty of ± 0.2 eV for the experimental reference (black) is marked by a gray band. MSE, MUE, and SD values for the set are tabulated.

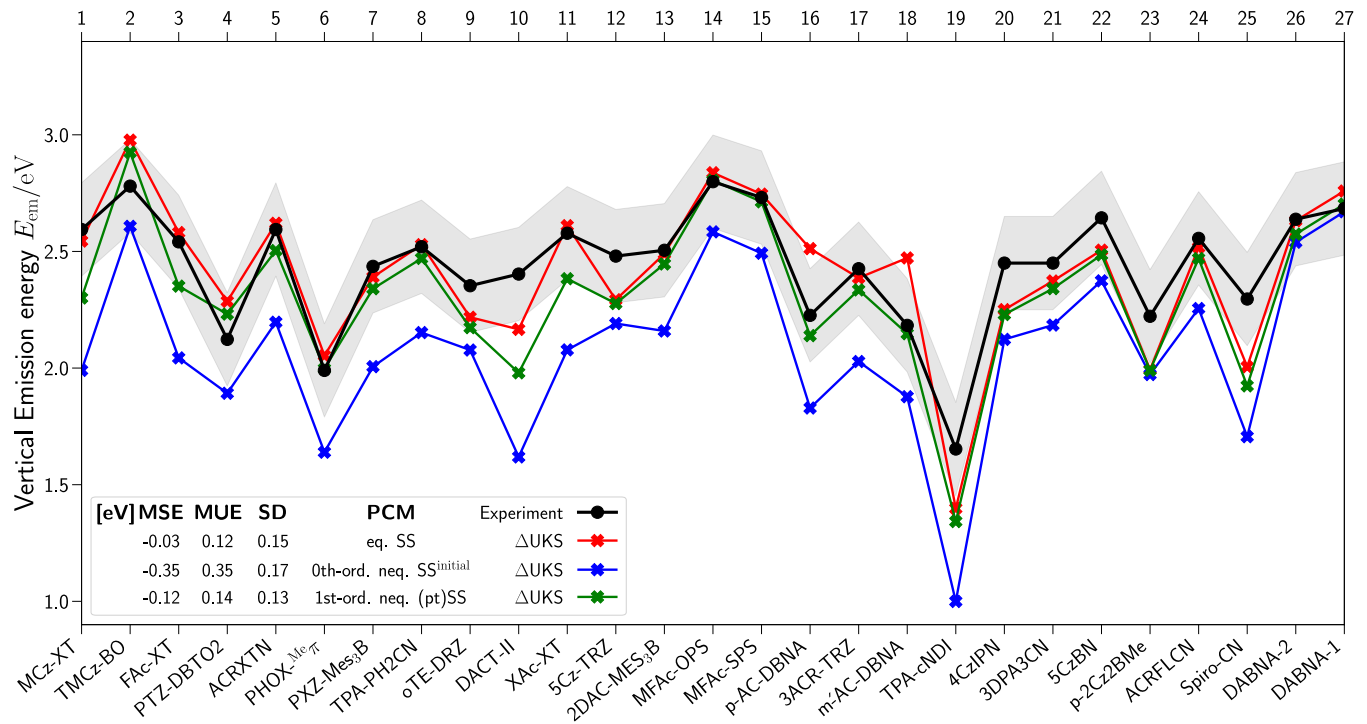


FIG. S5. Calculated emission energies E_{em} for different solvation models with Δ UKS/PCM using the OT-LRC- ω PBEh-D4 functional (dash-dotted lines) at the consistently optimized S_1 geometry. ϵ and n^2 were chosen for the measurement-specific solvent. An estimated uncertainty of ± 0.2 eV for the experimental reference (black) is marked by a gray band. MSE, MUE, and SD values for the set are tabulated.

C. Basis set effects

To investigate the effect of the basis set size on the emission energies, Figure S6 depicts E_{em} with TDA-DFT/ptSS-PCM and $\Delta\text{UKS}/\text{ptSS-PCM}$ using either the def2-SVP or def2-TZVPP basis set and the OT-LRC- $\omega\text{PBEh-D4}$ functional. In the case of TDA-DFT/ptSS-PCM, deviations between the double- ζ basis set used throughout the study and the triple- ζ basis set deviations are consistently below 0.1 eV, which is much less than the effect of solvation or functional choice. The same is true for the statistical measures. In the case of $\Delta\text{UKS}/\text{ptSS-PCM}$ deviations are a bit larger but still below 0.2 eV. The ensuing underestimation of the gap is still in the range of the functional choice. Hence, we conclude in line with our previous results that the small double- ζ basis set is sufficient in the present case concerning strong CT states in TADF emitters.[7, 8]

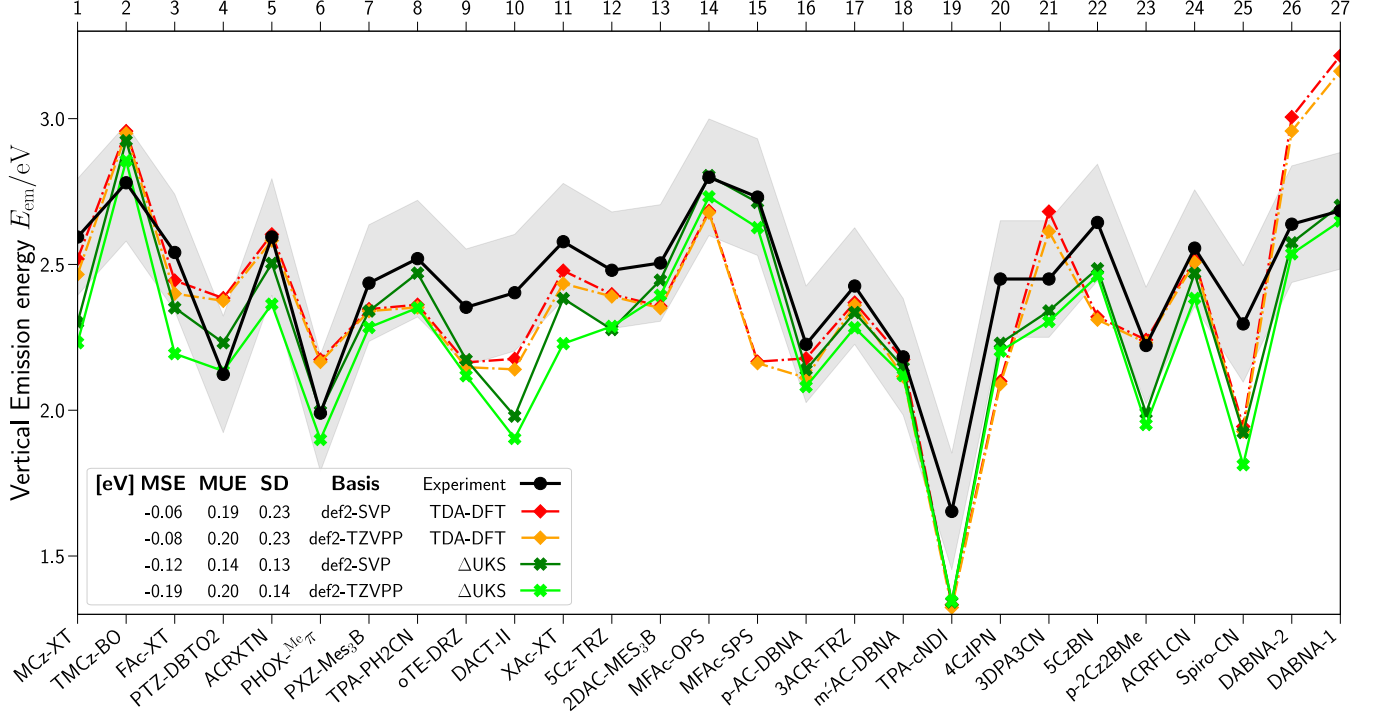


FIG. S6. Calculated emission energies E_{em} for different basis set sizes (def2-SVP and def2-TZVPP). Values are shown for the OT-LRC- $\omega\text{PBEh-D4}$ functional with TDA-DFT/ptSS-PCM (red) and $\Delta\text{UKS}/\text{ptSS-PCM}$ (green) at the consistently optimized S_1 geometry. ϵ and n^2 were chosen for a measurement-specific solvent. An estimated uncertainty of ± 0.2 eV for the experimental reference (black) is marked by the gray band. MSE, MUE, and SD values for the set are tabulated.

D. Statistical Measures

Statistical Measures of the N calculated values x_i with the reference values r_i

- Mean signed error (MSE): $\text{MSE} = \frac{1}{N} \sum_{i=1}^N (x_i - r_i)$
- Mean unsigned error (MUE): $\text{MUE} = \frac{1}{N} \sum_{i=1}^N |x_i - r_i|$
- Bessel Corrected standard deviation (SD): $\text{SD} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - r_i - \text{MSE})^2}$

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- [1] Epifanovsky, E.; Gilbert, A. T.; Feng, X.; Lee, J.; Mao, Y.; Mardirossian, N.; Pokhilko, P.; White, A. F.; Coons, M. P.; Dempwolff, A. L., et al. Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package. *The Journal of Chemical Physics* **2021**, *155*, 084801.
- [2] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [3] Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of Chemical Physics* **1999**, *110*, 6158.
- [4] Goerigk, L.; Grimme, S. A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions. *Physical Chemistry Chemical Physics* **2011**, *13*, 6670–6688.
- [5] Rohrdanz, M. A.; Herbert, J. M. Simultaneous benchmarking of ground- and excited-state properties with long-range-corrected density functional theory. *The Journal of Chemical Physics* **2008**, *129*, 034107.
- [6] Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M. A long-range-corrected density functional that performs well for both ground-state properties and time-dependent density functional theory excitation energies, including charge-transfer excited states. *The Journal of Chemical Physics* **2009**, *130*, 054112.
- [7] Kunze, L.; Hansen, A.; Grimme, S.; Mewes, J. M. PCM-ROKS for the Description of Charge-Transfer States in Solution: Singlet-Triplet Gaps with Chemical Accuracy from Open-Shell Kohn-Sham Reaction-Field Calculations. *Journal of Physical Chemistry Letters* **2021**, *12*, 8470–8480.
- [8] Froitzheim, T.; Grimme, S.; Mewes, J.-M. Either Accurate Singlet–Triplet Gaps or Excited-State Structures: Testing and Understanding the Performance of TD-DFT for TADF Emitters. *Journal of Chemical Theory and Computation* **2022**, *18*, 7702–7713.
- [9] Caldeweyher, E.; Bannwarth, C.; Grimme, S. Extension of the D3 dispersion coefficient model. *The Journal of Chemical Physics* **2017**, *147*, 034112.
- [10] Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A generally applicable atomic-charge dependent London dispersion correction. *The Journal of Chemical Physics* **2019**, *150*, 154122.
- [11] Friede, M.; Ehlert, S.; Grimme, S.; Mewes, J.-M. Do Optimally Tuned Range-Separated Hybrid Functionals Require a Reparametrization of the Dispersion Correction? It Depends. *Journal of Chemical Theory and Computation* **2023**, *19*, 8097–8107.
- [12] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics* **2005**, *7*, 3297–3305.
- [13] Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Physical Chemistry Chemical Physics* **2006**, *8*, 1057–1065.
- [14] Li, N.; Chai, D.; Chen, Z.; Zhou, C.; Ni, F.; Huang, Z.; Cao, X.; Xie, G.; Li, K.; Yang, C. Molecular engineering by σ -Bond spacer enables solution-processable host materials for TADF emitter towards high-performance OLEDs. *Chemical Engineering Journal* **2020**, *396*, 125276.
- [15] Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Physical Review Letters* **1984**, *52*, 997–1000.
- [16] Hirata, S.; Head-Gordon, M. Time-dependent density functional theory within the Tamm–Dancoff approximation. *Chemical Physics Letters* **1999**, *314*, 291–299.
- [17] Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic interaction of a solute with a continuum. A direct utilization of AB initio molecular potentials for the prevision of solvent effects. *Chemical Physics* **1981**, *55*, 117–129.
- [18] Herbert, J. M. Dielectric continuum methods for quantum chemistry. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2021**, *11*, e1519.
- [19] Improta, R.; Barone, V.; Scalmani, G.; Frisch, M. J. A state-specific polarizable continuum model time dependent density functional theory method for excited state calculations in solution. *The Journal of Chemical Physics* **2006**, *125*, 054103.
- [20] Improta, R.; Scalmani, G.; Frisch, M. J.; Barone, V. Toward effective and reliable fluorescence energies in solution by a new state specific polarizable continuum model time dependent density functional theory approach. *The Journal of Chemical Physics* **2007**, *127*, 074504.
- [21] Mewes, J. M.; Herbert, J. M.; Dreuw, A. On the accuracy of the general, state-specific polarizable-continuum model for the description of correlated ground- and excited states in solution. *Physical Chemistry Chemical Physics* **2017**, *19*, 1644–1654.
- [22] Tomasi, J.; Mennucci, B.; Cancès, E. The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level. *Journal of Molecular Structure: THEOCHEM* **1999**, *464*, 211–226.
- [23] Cammi, R.; Mennucci, B. Linear response theory for the polarizable continuum model. *The Journal of Chemical Physics* **1999**, *110*, 9877.
- [24] Gilbert, A. T. B.; Besley, N. A.; Gill, P. M. W. Self-Consistent Field Calculations of Excited States Using the Maximum Overlap Method (MOM). *The Journal of Physical Chemistry A* **2008**, *112*, 13164–13171.
- [25] Barca, G. M. J.; Gilbert, A. T. B.; Gill, P. M. W. Simple Models for Difficult Electronic Excitations. *Journal of Chemical Theory and Computation* **2018**, *14*, 1501–1509.
- [26] Van Voorhis, T.; Head-Gordon, M. A geometric approach to direct minimization. *Molecular Physics* **2002**, *100*, 1713–1721.
- [27] Gill, P. M. W.; Johnson, B. G.; Pople, J. A. A standard grid for density functional calculations. *Chemical Physics Letters* **1993**, *209*, 506–512.