

This is the peer reviewed version of the following article:

Understanding Aggregation-Induced Emission in Molecular Crystals: Insights from Theory / Presti, D., Wilbraham, L., Targa, C., Labat, F., Pedone, A., Menziani, M.C., Ciofini, I., Adamo, C.. - In: JOURNAL OF PHYSICAL CHEMISTRY. C. - ISSN 1932-7447. - 121:10(2017), pp. 5747-5752. [10.1021/acs.jpcc.7b00488]

Terms of use:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

29/06/2026 23:25

(Article begins on next page)

Understanding Aggregation Induced Emission in Molecular Crystals: Insights from Theory

Davide Presti, Liam Wilbraham, Cecilia Targa, Frédéric Labat, Alfonso Pedone, Maria Cristina Menziani, Ilaria Ciofini, and Carlo Adamo

J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.7b00488 • Publication Date (Web): 27 Feb 2017

Downloaded from <http://pubs.acs.org> on February 27, 2017

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Understanding Aggregation Induced Emission in Molecular Crystals: Insights from Theory

Davide Presti^{1,¶}, Liam Wilbraham^{2,¶}, Cecilia Targa,¹ Frédéric Labat², Alfonso Pedone¹, Maria Cristina Menziani¹, Ilaria Ciofini² and Carlo Adamo^{*2}

¹ *Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio-Emilia, 183 via G. Campi, I-41125 Modena, Italy.*

² *PSL Research University, Institut de Recherche de Chimie Paris IRCP, CNRS–Chimie ParisTech, 11 rue P. et M. Curie, F-75005 Paris 05, France.*

Abstract

Aggregation-induced emission can often be explained via the restriction of intramolecular rotation paradigm and/or excimer formation. The enhanced luminescence recently observed for aggregates of Fluorenone derivatives are no exception. In this work, however, we use a recently developed excited state electrostatic embedding technique to demonstrate that enhanced emission in diphenylfluorenone can be rationalized by considering a single-molecule process, in which the field induced by the crystalline environment at the excited state enhances the relative brightness of otherwise poorly emissive states, resulting in both enhanced fluorescence and a substantial bathochromic shift when compared with emission in dilute solution.

[¶] DP and LW contributed equally to this work. *Corresponding Authors: carlo.adamo@chimie-paristech.fr

1. Introduction

In most cases, the bright fluorescence observed in chromophores in dilute solutions is absent upon the aggregation or precipitation of the same chromophore, where self-quenching triggered by intermolecular interactions such as π - π stacking renders the system non-fluorescent.¹ This aggregation-caused-quenching (ACQ) poses a substantial challenge to the design and development of solid-state light-emitting devices for applications such as biological and chemical sensing and organic light-emitting diodes.²⁻⁶ A phenomenon which can be described as the mirror-image of this effect can, however, be observed in a special class of materials that exhibit weak or no fluorescence in dilute solution, yet demonstrate strong fluorescence in the solid-state. This is known as aggregation induced emission (AIE),⁷ and is generally observed in chromophores comprising rigid moieties, which are capable of rotation relative to a relatively inflexible core.⁸ AIE is facilitated by the steric interactions introduced in the solid-state which reduce the rotational flexibility of the rotator moieties (the so-called Restriction of Intramolecular Rotation, RIR) and subsequently block potentially fast deactivation pathways otherwise fully accessible in dilute solution.^{7,9-12}

From a theoretical point of view, attempts have been made to rationalize this process via the calculation of potential energy surfaces along rotational trajectories and the analysis of the non-radiative decay rates along these pathways.^{13,14} While this concept can readily explain AIE observed in chromophores such as trimethylsilole,¹⁵ in which the emission of the aggregate is of a similar wavelength to that of the molecule in solution, it is not sufficient to explain large solvatochromic-like effects observed in some AIE chromophores.

The concomitant brightening and significant bathochromic shift of emission band maxima during the aggregation of such chromophores is usually attributed to the formation of excimers. This is

1
2
3 experimentally substantiated by an apparent broadening of the emission band itself, along with an
4
5 increased excited state lifetime observed via time resolved fluorescence techniques.¹⁶
6
7

8 2,7-diphenylfluorenone (DPF) is one such chromophore, demonstrating more than a 150 nm red
9
10 shift of the emission band after aggregation, which is attributed to excited state excimer
11
12 formation.¹⁶⁻¹⁸ This work will demonstrate, however, that AIE in DPF arises from a single-
13
14 molecule process rather than the formation of excimers. Using a recently developed excited state
15
16 electrostatic embedding model as an approximation of the solid state environment,¹⁹ it will be
17
18 shown that the field induced by the crystalline environment can enhance the relative brightness of
19
20 otherwise poorly emissive states in DPF, resulting in both enhanced fluorescence and a
21
22 substantial bathochromic shift when compared with emission in dilute solution.
23
24
25
26
27
28

29 **2. Computational Details**

30
31 *Single molecule calculations.* DFT and TDDFT calculations have been used to investigate the
32
33 ground and excited state properties of a single DPF molecule in vacuum and in THF solution.
34

35
36 The latter were described by using the Conductor-like Polarizable continuum solvation Model
37
38 (C-PCM) in the linear response formulation.²⁰
39

40
41 Ground and excited state geometry optimizations and absorption/emission energies have been
42
43 performed using both B3LYP^{21,22} and CAM-B3LYP²³ functionals coupled with the 6-31+G(d,p)
44
45 basis set which represents the best compromise between cost and quality of the geometrical
46
47 parameters (see table S.2 of SI). All these calculations have been carried out with the Gaussian09
48
49 suite of programs.²⁴
50
51

52
53 *Periodic Solid state calculations.* In order to determine the equilibrium atomic positions and unit
54
55 cell parameters for subsequent embedding techniques, ground-state calculations have been
56
57 carried out on bulk DPF, employing the parallel version of the CRYSTAL09 package.^{25,26} With
58
59
60

1
2
3 the purpose of obtaining an electronic ground-state structurally as close as possible to the
4 experimental one, we performed a dispersion-corrected B3LYP-D*²⁷/6-31G(d,p) full
5 optimization (cell and atomic positions) of the solid crystalline system, shown in **Figure S.3** of
6 the Supporting Information (SI) (168 atoms/cell, $Cmc2_1$, $Z=4$). In such a case, diffuse functions
7 were not utilized to avoid basis-set linear dependence issues. The Monkhorst-Pack grid was set to
8 6 k -points within the Irreducible Brillouin Zone. An extra-large DFT grid (75 radial and 974
9 angular points) was chosen. The tolerances on Coulomb and exchange bielectronic integrals were
10 set to 10^{-9} , 10^{-9} , 10^{-9} , 10^{-9} , 10^{-18} a.u.
11
12
13
14
15
16
17
18
19
20
21

22 In order to determine excited state properties of crystalline DPF, the QM/QM' ONIOM and the
23 Self-Consistent Ewald embedding methods have been used.
24
25

26 *ONIOM QM/QM' calculations.* In this approach a sufficiently large cluster is cut from a crystal
27 supercell and treated at the QM/QM' level in which the high level region consists of the central
28 single DPF molecule or a central dimer as shown in Figure 1a and S.4 of ESI, respectively.
29
30
31
32

33 The low-level region includes 20 DPF molecules for the monomer model (**Figure 1a**), whereas it
34 includes 20 and 22 DPF molecules (the nearest-neighbors molecules, within a range of 3.8-4.0 Å)
35 for the two dimer models considered, **Dimer 1** and **Dimer 2**, respectively (see SI, **Figure S.4**).
36
37
38
39

40 Monomer and dimer vertical absorption energies have been computed at the TD-DFT/6-
41 31+G(d,p):HF/STO-3G level of theory, at the optimized crystalline geometry (*vide supra*)
42 whereas the emission spectra were computed by optimizing at the same level of theory the
43 (lowest) bright excited singlets (S_1 and S_3 states) involved in the fluorescent emission observed
44 experimentally. The S_2 state was not considered since, in every case, it was computed to be
45 nearly/totally a *dark* state (oscillator strength $f=0.000$ a.u.) (see **Table S5**). As DFT
46 approximations, B3LYP and CAM-B3LYP functionals were considered for the high-level QM
47 region. Following previous investigations²⁸⁻³⁰ the low level region was treated at the Hartree-
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 Fock (HF) level coupled with the Slater-type STO-3G minimal basis set since it provides
4 Mulliken charges similar to that obtained with more accurate calculations.
5
6

7
8 *Self-Consistent Ewald embedding calculations.* The solid state environment has also been
9 modelled using the so-called Self-Consistent Ewald approach (SC-Ewald), previously developed
10 by some of us.¹⁹ Briefly, this process seeks to approximate the excited state crystalline
11 environment via a large array of point charges while, at the same time, performing a charge
12 fitting process to reproduce the infinite electrostatic potential of the fully periodic system, using
13 the approach first developed by Derenzo and co-workers.³¹
14
15

16
17 The charge array was composed of a 5×5×5 supercell, in order to obtain a cube-like distribution
18 of point charges, giving a total of approximately 11000 point charges. For the charge fitting
19 procedure, the fixed charge zone (Zone 2, see **Figure 1b**) was set to an origin-centered sphere
20 containing 1500 atoms in order to ensure the QM region (Zone 1) is not close to the ‘outside
21 wall’ of Zone 2. The resulting fitted charges in Zone 3 produced an adequate root mean square
22 (RMS) error of the Ewald potential within Zone 1 of less than 0.1 μV.
23
24

25
26 To model the crystalline environment at the excited state, this charge array was recomputed self-
27 consistently using the Mulliken charges derived from the electronic density of the excited state of
28 interest (S₁ and S₃ states in this case), applying a convergence criterion of 0.001 |e-| with respect
29 to the mean average deviation of the computed charges in Zone 1. In order to avoid numerical
30 instabilities,³² the SC-Ewald procedure was carried out using a reduced basis set (6-31G), before
31 reverting to the full basis set (6-31+G(d,p)) for the calculation of optical absorption and emission
32 properties within the generated charge background.
33
34
35

36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 **3. Results and Discussion**

54
55 Following the experimental interpretation of excimer formation as the root cause of AIE in DPF,
56 absorption features were first determined for two sets of dimers found in crystalline DPF. From
57
58
59
60

1
2
3 Figure 2, it can be clearly observed that, regardless of the dimer chosen, the effect on the
4
5 calculated absorption spectrum - with respect to that of the monomer - is negligible. This
6
7 observation also holds when the solid state environment is approximated using the ONIOM
8
9 method. Together, these results show that, at least in the vertical absorption regime, the
10
11 intermolecular coupling is not sufficient to alter the observed photophysical properties either in
12
13 terms of energy or absorption intensity. From these results, it is then necessary to consider
14
15 alternative mechanisms to rationalize the AIE behaviour of DPF. In the following, starting from a
16
17 monomer picture, it will be shown that both the absorption and emission spectra of aggregated
18
19 DPF can be explained via a single-molecule process, facilitated by interactions with the
20
21 crystalline environment at the excited state.
22
23
24
25
26

27 Figure 3 shows the UV-Visible absorption spectra computed at B3LYP and CAM-B3LYP level
28
29 for the DPF monomer in vacuum, THF (implicit) solution and with the ONIOM QM/QM' and
30
31 SC-Ewald embedding protocols.
32
33

34 At first glance, a qualitative accuracy of both functionals for the overall spectral band shapes can
35
36 be observed, with respect to the experimental counterpart in concentrated (60 μM) THF solution
37
38 (Figure 1g of the experimental paper¹⁶) – where DPF is supposed to be emissive due to being in
39
40 an aggregated form. Also, an almost quantitative spectral characterization is provided by B3LYP
41
42 in terms of λ_{max} wavelengths, relative band intensities and band shapes. It should be noted that in
43
44 the following, absorption spectra will be compared with those in concentrated THF solution (60
45
46 μM), whereas λ_{max} refer to those available, i.e. obtained in THF/water (20 μM) which provide,
47
48 nonetheless, the same optical transitions.
49
50
51

52 In more detail, the main transitions found experimentally (Table 1 of Ref.¹⁶) – corresponding to
53
54 4.34 eV, 3.64 eV and 2.63 eV (286 nm, 341 nm, and 471 nm) – are quite well reproduced. A
55
56 sizable bathochromic (hypsochromic) shift is observed with B3LYP (CAM-B3LYP) for the high
57
58
59
60

1
2
3 energy/most intense π - π^* transition located experimentally at 4.34 eV which is, however, of little
4
5 interest for potential AIE mechanisms, due to the very low probability of populating the
6
7 associated singlet excited state ($S_5 \leftarrow S_0$).
8

9
10 Moving towards lower energy transitions, a better description is given by B3LYP for the two
11
12 convoluted bands at ca. 3.84 eV ($S_3 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions with π - π^* character), whereas
13
14 CAM-B3LYP predicts hypsochromically shifted transitions. It is worth noting here that the
15
16 vibronic band shape observed in the experimental spectrum is not accounted for within the
17
18 current computational protocol.³³⁻³⁷
19

20
21 A broad and weak absorption band at ca. 2.63 eV (471 nm, not indicated in the experimental
22
23 work for the 20 μ M THF solution, but nonetheless producing a distinguishable non-zero
24
25 absorption signal, see Figure 1c of Ref.¹⁶) arises in the computed B3LYP spectra, and it is
26
27 consistent with the weak absorption of the first (HOMO-LUMO, $S_1 \leftarrow S_0$) transition, possessing
28
29 CT character. Here, the electronic effects from the use of different structural and environmental
30
31 descriptions of DPF highlight that: i) as expected, B3LYP gives, in general, a better prediction of
32
33 the $S_1 \leftarrow S_0$ wavelength, compared to experiment, but this could be due to the limited through-
34
35 space character of this transition, whereas ii) CAM-B3LYP, though sizably underestimating the
36
37 λ_{max} of all transitions, it gives a more homogeneous and systematic shift by using the different
38
39 models. Moreover, recalling that such functional is known to perform well in describing
40
41 transitions with a CT character,^{23,38} we expect it to provide reasonable values for vertical
42
43 emission with respect to B3LYP, which usually predicts overestimated transitions. iii) A
44
45 bathochromic shift from 376 nm to 397 nm is associated to the electronic effects occurring when
46
47 passing from vacuum to implicit solvation, to ONIOM QM/QM' and finally to SC-Ewald
48
49 embedding (CAM-B3LYP). Such a trend goes towards the experimental transition of 471 nm
50
51
52
53
54
55
56
57
58
59
60

1
2
3 (though graphically, the λ_{\max} is located even closer at ca. 440 nm); iv) the same magnitude of
4 bathochromic shift is observed for B3LYP, going from 452 nm to 468 nm.
5
6

7
8 In the following, it will be shown that the enhanced emission observed upon aggregation of DPF
9 can be rationalized considering only a single molecule, with the condition that one must account
10 for the influence of the solid state environment. **Figure 4** shows the calculated and experimental
11 emission spectra. Experimentally, it is observed that concentrated solutions of DPF dissolved in
12 tetrahydrofuran produce two distinct emission bands. The first band, at 360 nm (3.44 eV), is
13 attributed to emission from isolated molecules of DPF in solution (E_{SOL}) whereas the second
14 band, at 534 nm (2.32 eV), is attributed to emission from the DPF aggregate (E_{AGG}). Importantly,
15 E_{AGG} is not observed in low concentration (20 μM) THF solutions of DPF, due to the absence of
16 aggregate formation.¹⁶ In the following, we approximate the aggregated form of DPF as a perfect
17 crystal. Due to the near-identical emission behavior observed experimentally for powdered and
18 aggregated DPF and the precipitate-like nature of the aggregate, we deem this approximation to
19 be viable.
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

36 From calculations performed on a single molecule of DPF, both in THF solution and by
37 approximating the crystalline environment, E_{SOL} can be attributed to radiative emission from the
38 S_3 state, which corresponds to a $\pi-\pi^*$ excited state (**Figure 3**). From Figure 4 it can be seen that,
39 of all of the models tested E_{SOL} is best reproduced, albeit with a marginal blue shift, using the
40 THF solvent model which results in a calculated emission energy approximately 0.2 eV from the
41 experimental value. The solid-state models, however, yield a significantly blue shifted (by 0.5
42 eV) emission maximum relative to experiment. Given the superior performance of the THF
43 model, these results support that E_{SOL} is indeed a result of emission from isolated monomers of
44 DPF in solution. Additionally, it can be seen that both solid state models – ONIOM QM/QM' and
45 SC-Ewald – produce similar emission bands. This is significant, as it is an indication that the
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 close-range electrostatic interactions are well reproduced by the SC-Ewald approach, despite
4
5 relying on simple point charges to approximate the crystalline environment. Furthermore,
6
7 although SC-Ewald approximates the excited state crystalline potential while ONIOM
8
9 approximates the ground state environment, due to the small spatial difference in density between
10
11 the ground state and S_3 excited state it is to be expected that the ground and excited state
12
13 potentials – and thus the resulting emission energies – will be similar.
14
15

16
17 Now considering E_{AGG} – a result of emission from the S_1 CT excited state ($S_1 \rightarrow S_0$) – all models
18
19 produce emission energies comparable with experiment, with errors of just 0.11, 0.12 and 0.05
20
21 eV for THF, ONIOM and SC-Ewald, respectively. In contrast to E_{SOL} , ONIOM and SC-Ewald
22
23 yield somewhat different emission energies for E_{AGG} , with SC-Ewald producing an emission
24
25 energy that is 0.15 eV red-shifted with respect to ONIOM. Again, this is significant and
26
27 highlights the state-specific nature of the excited state crystalline potential generated by SC-
28
29 Ewald. Naturally, the pronounced charge transfer character of the S_1 excited state results in a
30
31 marked rearrangement of the electronic density and, consequently, a non-negligible alteration to
32
33 the surrounding embedding potential, which is reflected in the calculated emission energy.
34
35
36

37
38 Perhaps more interesting within the context of AIE is the difference in relative intensity between
39
40 E_{SOL} and E_{AGG} produced by each model. In the case of THF, the weak emission from the S_1 state
41
42 relative to that of the S_3 state is consistent with the lack of emission intensity observed
43
44 experimentally for DPF in THF solution. Upon introducing the solid-state environment via the
45
46 ONIOM model, a marginal enhancement of E_{AGG} can be noticed, in terms of brightness, although
47
48 this is not of a sufficient magnitude to account for the experimentally measured enhanced
49
50 emission of the aggregate. However, when accounting for the excited state crystalline potential as
51
52 produced by SC-Ewald, a remarkable agreement with the experimental spectrum is observed, and
53
54 the enhanced emission as a result of the aggregation is recovered. In this way, the potentially
55
56
57
58
59
60

1
2
3 non-negligible effects of not only the long-range electrostatic interactions but also the excited
4 solid state potential are evident. Crucially, using this model it can be shown that both the large
5 red-shift and enhanced emission intensity upon aggregation of DPF can be rationalized with a
6 single molecule, without considering intermolecular electronically excited states or excimer
7 formation. Notably, this is in contrast to the previous experimental interpretation, which relies on
8 the formation of so-called “static excimers” – comprising dimers of DPF – to account for the 150
9 nm red-shift upon aggregation.
10
11
12
13
14
15
16
17
18

19 **4. Conclusions**

20
21 Our results demonstrate how, generally, modelling different environmental effects to a sufficient
22 quality is crucial for the understanding and reproduction of experimental observations within the
23 context of AIE. More specifically, in the case of DPF, it has been shown that the often-cited
24 restriction of intramolecular rotation paradigm provides an incomplete picture of the AIE process
25 in this particular case. Instead, a theoretical analysis has shown that the concomitant red-shift and
26 fluorescence-enhancement upon aggregation of DPF monomers in solution is due to an
27 environmentally driven process, relying on both short- and long-range excited state electrostatic
28 interactions between a single molecule and its surroundings within the aggregate. We therefore
29 suggest that the excited-state field of the environment enables the enhanced emission of
30 otherwise poorly emissive, low-lying excited states and leads to an observed intense aggregate
31 emission at lower wavelength with respect to solution. Interestingly, this lies in contrast to the
32 previous interpretation of experimental results, which cite the formation of so-called “static
33 excimers”. We envisage that, for other reported cases of AIE accompanied by a significant
34 changes in emission maxima, this protocol could be generally applied as a tool not only to
35 understand, but to aid in the design of better-performing materials by providing a means of
36 accommodating interaction with complex environments.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Supporting Information. Molecular scheme and crystalline structure of DPF, main structural parameters, structure of the two dimers' clusters and their calculated UV-Vis. absorption spectra, Complete References 10, 24, 25

Acknowledgements

DP and LW contributed equally to this work. Computational resources for this work were granted by the 'Projet 100339' (2015) at GENCI-IDRIS (Orsay, France).

References

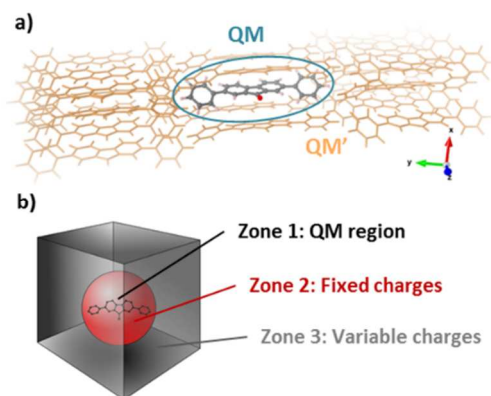
- (1) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.
- (2) El'tsov, A. *Organic Photochromes*, Plenum.; New York, 1990.
- (3) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Topics in Applied Chemistry; Plenum Press: New York, 1999.
- (4) Tang, C. W.; VanSlyke, S. A. Organic Electroluminescent Diodes. *Appl. Phys. Lett.* **1987**, *51*, 913–915.
- (5) Zhao, Z.; Chen, S.; Deng, C.; Lam, J. W. Y.; Chan, C. Y. K.; Lu, P.; Wang, Z.; Hu, B.; Chen, X.; Lu, P.; et al. Construction of Efficient Solid Emitters with Conventional and AIE Luminogens for Blue Organic Light-Emitting Diodes. *J. Mater. Chem.* **2011**, *21*, 10949–10956.
- (6) Ding, D.; Li, K.; Liu, B.; Tang, B. Z. Bioprobes Based on AIE Fluorogens. *Acc. Chem. Res.* **2013**, *46*, 2441–2453.
- (7) Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
- (8) Shustova, N. B.; Ong, T.-C.; Cozzolino, A. F.; Michaelis, V. K.; Griffin, R. G.; Dincă, M. Phenyl Ring Dynamics in a Tetraphenylethylene-Bridged Metal–Organic Framework: Implications for the Mechanism of Aggregation-Induced Emission. *J. Am. Chem. Soc.* **2012**, *134*, 15061–15070.
- (9) Kasha, M. Energy Transfer Mechanisms and the Molecular Exciton Model for Molecular Aggregates. *Radiat. Res.* **1963**, *20*, 55–70.

- 1
2
3 (10) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu,
4 Y.; Zhu, D.; et al. Aggregation-Induced Emission of 1-Methyl-1,2,3,4,5-Pentaphenylsilole.
5 *Chem. Commun.* **2001**, No. 18, 1740–1741.
6
7
8 (11) Zhao, Z.; He, B.; Tang, B. Z. Aggregation-Induced Emission of Siloles. *Chem. Sci.* **2015**,
9 6, 5347–5365.
10
11 (12) Padalkar, V. S.; Seki, S. Excited-State Intramolecular Proton-Transfer (ESIPT)-Inspired
12 Solid State Emitters. *Chem. Soc. Rev.* **2015**, 45, 169–202.
13
14 (13) Wu, Q.; Deng, C.; Peng, Q.; Niu, Y.; Shuai, Z. Quantum Chemical Insights into the
15 Aggregation Induced Emission Phenomena: A QM/MM Study for Pyrazine Derivatives. *J.*
16 *Comput. Chem.* **2012**, 33, 1862–1869.
17
18 (14) Wu, Q.; Peng, Q.; Niu, Y.; Gao, X.; Shuai, Z. Theoretical Insights into the Aggregation-
19 Induced Emission by Hydrogen Bonding: A QM/MM Study. *J. Phys. Chem. A* **2012**, 116, 3881–
20 3888.
21
22 (15) Li, Z.; Dong, Y. Q.; Lam, J. W. Y.; Sun, J.; Qin, A.; Häußler, M.; Dong, Y. P.; Sung, H.
23 H. Y.; Williams, I. D.; Kwok, H. S.; et al. Functionalized Siloles: Versatile Synthesis,
24 Aggregation-Induced Emission, and Sensory and Device Applications. *Adv. Funct. Mater.* **2009**,
25 19, 905–917.
26
27 (16) Yuan, M.-S.; Wang, D.-E.; Xue, P.; Wang, W.; Wang, J.-C.; Tu, Q.; Liu, Z.; Liu, Y.;
28 Zhang, Y.; Wang, J. Fluorenone Organic Crystals: Two-Color Luminescence Switching and
29 Reversible Phase Transformations between Π - π Stacking-Directed Packing and Hydrogen Bond-
30 Directed Packing. *Chem. Mater.* **2014**, 26, 2467–2477.
31
32 (17) Yuan, M.-S.; Du, X.; Xu, F.; Wang, D.-E.; Wang, W.-J.; Li, T.-B.; Tu, Q.; Zhang, Y.; Du,
33 Z.; Wang, J. Aggregation-Induced Bathochromic Fluorescent Enhancement for Fluorenone Dyes.
34 *Dyes Pigments* **2015**, 123, 355–362.
35
36 (18) Xu, F.; Wang, H.; Du, X.; Wang, W.; Wang, D.-E.; Chen, S.; Han, X.; Li, N.; Yuan, M.-
37 S.; Wang, J. Structure, Property and Mechanism Study of Fluorenone-Based AIE Dyes. *Dyes*
38 *Pigments* **2016**, 129, 121–128.
39
40 (19) Wilbraham, L.; Adamo, C.; Labat, F.; Ciofini, I. Electrostatic Embedding To Model the
41 Impact of Environment on Photophysical Properties of Molecular Crystals: A Self-Consistent
42 Charge Adjustment Procedure. *J. Chem. Theory Comput.* **2016**, 12, 3316–3324.
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (20) Corni, S.; Cammi, R.; Mennucci, B.; Tomasi, J. Electronic Excitation Energies of
4 Molecules in Solution within Continuum Solvation Models: Investigating the Discrepancy
5 between State-Specific and Linear-Response Methods. *J. Chem. Phys.* **2005**, *123*, 134512.
6
7
8 (21) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J.*
9 *Chem. Phys.* **1993**, *98*, 5648–5652.
10
11 (22) Lee, C.; Yang, W.; Parr, R. Development of the Colle-Salvetti Correlation-Energy
12 Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, *37*, 785–789.
13
14 (23) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–correlation Functional
15 Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
16
17 (24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J.
18 R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. *Gaussian 09 Revision D.01*;
19 Wallingford CT, 2009.
20
21 (25) R. Dovesi; V. R. Saunders; C. Roetti; R. Orlando; C. M. Zicovich-Wilson; F. Pascale; K.
22 Doll; N. M. Harrison; B. Civalleri; I. J. Bush; et al. *CRYSTAL09 User's Manual*; Università di
23 Torino: Torino, 2010.
24
25 (26) Dovesi, R.; Orlando, R.; Civalleri, B.; Roetti, C.; Saunders, V. R.; Zicovich-Wilson, C. M.
26 CRYSTAL: A Computational Tool for the Ab Initio Study of the Electronic Properties of
27 Crystals. *Z. Krist.* **2005**, *220*, 571–573.
28
29 (27) Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. B3LYP Augmented
30 with an Empirical Dispersion Term (B3LYP-D*) as Applied to Molecular Crystals.
31 *Crystengcomm* **2008**, *10*, 405–410.
32
33 (28) Presti, D.; Labat, F.; Pedone, A.; Frisch, M. J.; Hratchian, H. P.; Ciofini, I.; Menziani, M.
34 C.; Adamo, C. Computational Protocol for Modeling Thermochromic Molecular Crystals:
35 Salicylidene Aniline As a Case Study. *J. Chem. Theory Comput.* **2014**, *10*, 5577–5585.
36
37 (29) Presti, D.; Labat, F.; Pedone, A.; Frisch, M. J.; Hratchian, H. P.; Ciofini, I.; Cristina
38 Menziani, M.; Adamo, C. Modeling Emission Features of Salicylidene Aniline Molecular
39 Crystals: A QM/QM' Approach. *J. Comput. Chem.* **2016**, *37*, 861–870.
40
41 (30) Presti, D.; Pedone, A.; Ciofini, I.; Labat, F.; Menziani, M. C.; Adamo, C. Optical
42 Properties of the Dibenzothiazolylphenol Molecular Crystals through ONIOM Calculations: The
43 Effect of the Electrostatic Embedding Scheme. *Theor. Chem. Acc.* **2016**, *135*, 1–11.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (31) Klintonberg, M.; Derenzo, S. E.; Weber, M. J. Accurate Crystal Fields for Embedded
4 Cluster Calculations. *Comput. Phys. Commun.* **2000**, *131*, 120–128.
5
6 (32) Weber, J.; Günne, J. S. auf der. Calculation of NMR Parameters in Ionic Solids by an
7 Improved Self-Consistent Embedded Cluster Method. *Phys. Chem. Chem. Phys.* **2009**, *12*, 583–
8 603.
9
10 (33) Bloino, J.; Biczysko, M.; Santoro, F.; Barone, V. General Approach to Compute
11 Vibrationally Resolved One-Photon Electronic Spectra. *J. Chem. Theory Comput.* **2010**, *6*, 1256–
12 1274.
13
14 (34) Baiardi, A.; Bloino, J.; Barone, V. General Time Dependent Approach to Vibronic
15 Spectroscopy Including Franck–Condon, Herzberg–Teller, and Duschinsky Effects. *J. Chem.*
16 *Theory Comput.* **2013**, *9*, 4097–4115.
17
18 (35) Jacquemin, D.; Brémond, E.; Planchat, A.; Ciofini, I.; Adamo, C. TD-DFT Vibronic
19 Couplings in Anthraquinones: From Basis Set and Functional Benchmarks to Applications for
20 Industrial Dyes. *J. Chem. Theory Comput.* **2011**, *7*, 1882–1892.
21
22 (36) Jacquemin, D.; Brémond, E.; Ciofini, I.; Adamo, C. Impact of Vibronic Couplings on
23 Perceived Colors: Two Anthraquinones as a Working Example. *J. Phys. Chem. Lett.* **2012**, *3*,
24 468–471.
25
26 (37) Muniz-Miranda, F.; Pedone, A.; Battistelli, G.; Montalti, M.; Bloino, J.; Barone, V.
27 Benchmarking TD-DFT against Vibrationally Resolved Absorption Spectra at Room
28 Temperature: 7-Aminocoumarins as Test Cases. *J. Chem. Theory Comput.* **2015**, *11*, 5371–5384.
29
30 (38) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. Long-Range Charge-Transfer Excited
31 States in Time-Dependent Density Functional Theory Require Non-Local Exchange. *J. Chem.*
32 *Phys.* **2003**, *119*, 2943–2946.
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 **Figure 1.** Schematic representation of the solid state models used in this work. (a) Solid state
4 modeled using a two-level ONIOM QM/QM' scheme, with the low-level region including 20
5 nearest-neighbor molecules. (b) Solid state modeled using the ground (absorption) or excited
6 state (emission) potentials generated by the SC-Ewald procedure, outlined in Ref.¹⁹ Fitted
7 charges (grey cube, Zone 3) are used to reproduce the excited state infinite crystalline potential
8 within a given zone (red ball, Zone 2). Within this zone, a quantum-mechanically treated cluster
9 is placed (black molecule, Zone 1).



1
2
3
4 **Figure 2.** (a) Absorption spectra of dimer clusters extracted from the crystalline structure of DPF,
5 computed at the CAM-B3LYP level of theory for two different dimer configurations: **Dimer 1**
6 (b) and **Dimer 2** (c). These spectra have been obtained both in vacuum (solid lines) and using the
7 ONIOM QM/QM' cluster model (dotted lines). A FWHM value of 0.35 eV is used throughout.
8 For comparison, analogous calculations performed on monomers and the experimental
9 spectrum¹⁶ are given.

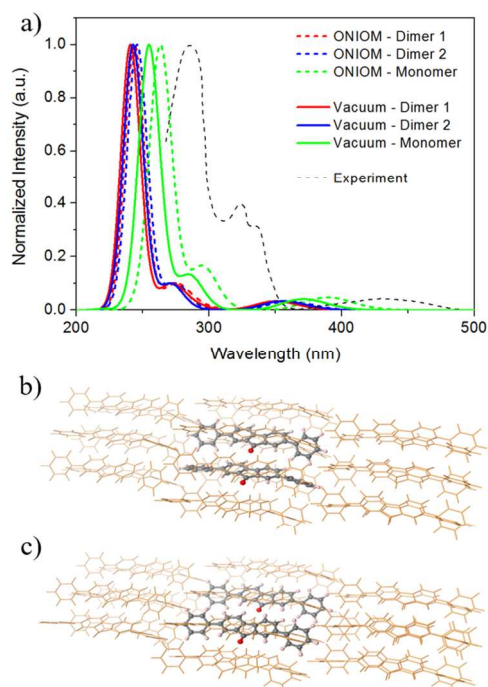
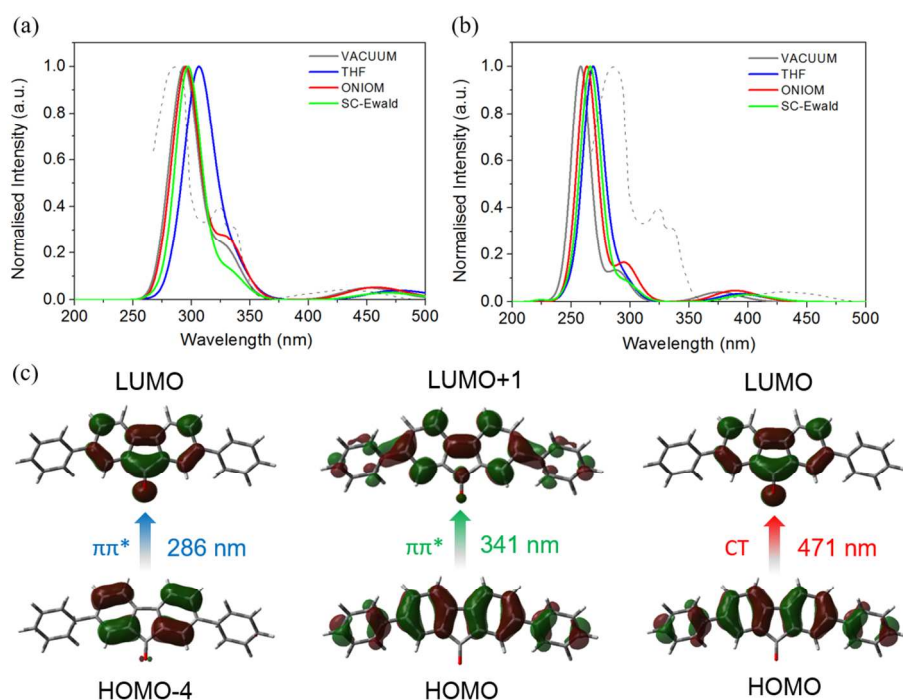
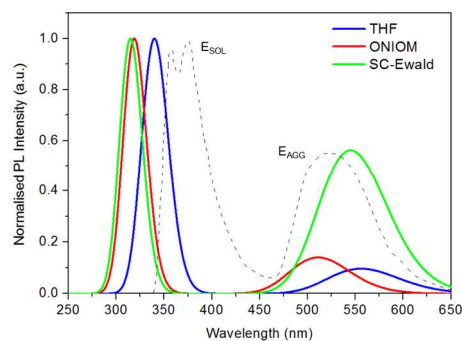


Figure 3. Calculated absorption spectra of DPF at the (a) B3LYP and (b) CAM-B3LYP level, adopting four different models to approximate the environment: i) in vacuum, ii) in THF, using implicit solvation, iii) in the solid state using an ONIOM QM/QM' model and iv) in the solid state using the ground state embedding potential as determined by the SC-Ewald procedure. A FWHM value of 0.35 eV is used throughout. The experimental absorption spectrum¹⁶ is also shown (dashed lines). (c) Assignment and molecular orbitals involved in first three bright transitions ($S_1 \leftarrow S_0$, $S_3 \leftarrow S_0$, and $S_5 \leftarrow S_0$) of DPF (orbital isocontour value of 0.03 a.u.) along with the experimental absorption energies of the relevant bands.



1
2
3
4 **Figure 4.** Calculated emission spectra of both $S_1 \rightarrow S_0$ and $S_3 \rightarrow S_0$ transitions at the CAM-B3LYP
5 level: i) in THF (implicit solvation, C-PCM), ii) in the solid state using ONIOM QM/QM' and
6 iii) in the solid state using the SC-Ewald embedding procedure. A FWHM value of 0.35 eV is
7 used throughout. The experimental spectrum is also shown (dashed lines). E_{SOL} and E_{AGG} indicate
8 experimental emission bands attributed to dissolved and aggregated DPF respectively. All spectra
9 are normalized with respect to E_{AGG} .
10
11
12
13
14
15



TOC GRAPHICS

