Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for "Organic compounds for solid state luminescence enhancement/ Aggregation induced emission: a theoretical perspective"

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TPE-MRh: calculation of Huang-Rhys factors in solid state

To investigate of TPE-MRh fluorescence in solid state, three main steps were performed. Firstly the crystal polymorphs representing the lowest energy molecular packings more likely to be found in the experimental samples were searched. With these structures, point-charge distributions approximating the periodic potential felt by the fluorescent unit (a single molecule, in this case) in the crystalline environment generated by molecular packing have been calculated using the Ewald approach. In a second step, these distributions have been used as background embeddings in TD-DFT calculations to obtain the vertical transition energies of TPE-MRh in crystalline phase. The computational details and results of the calculations of these first two steps are reported and discussed in ref.[1]. A third step has consisted in performing additional calculations on a supercell of 24 molecules from the polymorph structure with the lowest energy according to periodic DFT calculations described in[1] , a structure belonging to the $Pna2_1$ space group labelled as 'polymorph 1' in the same ref.
Atomic coordinates of this molecular cluster have been used as input for a two-level calculation following the ONIOM scheme[2] as implemented in Gaussian16[3].
In order to obtain reasonably accurate relaxed structures and vibrational frequencies for the ground and the excited states (first singlet, S_1) of the luminescent unit as found in polymorph 1, a single molecule (74 atoms) within the cluster has been selected approximately at the center of the cluster and has been defined as high ONIOM layer described with a B3LYP level in combination with a specific basis set optimized for calculations in solid state, reported below, and Grimme's empirical dispersion with Becke-Johnson damping[4]. The other molecules in the supercell have been grouped in the low ONIOM layer (1702 atoms, for a total of 1776 atoms) and have been frozen at the positions extracted from the optimized crystal structure during the calculation. Their electronic structure has been described at Hartree-Fock level in combination with a small split-valence basis set (3-21G*) including polarization functions on heavy atoms. The vibrational analysis on the resulting geometries has ensured that the stationary points obtained were indeed minima at the level of theory chosen for both ground and excited states. The computed harmonic frequencies have been used to calculate the Huang-Rhys factors[5] in the adiabatic shift approximation, i.e., the frequencies at the excited state S_1, describing the 'local' shape of the potential energy surface in the harmonic approximation, are assumed to be the same in the initial (S1) and final (S0) state of the transition and the difference between the two minima is assumed to be a shift in the space of nuclear degrees of freedom.

Below we report the fractional coordinates of the optimized unit cell for polymorph 1 (see ref. [1] for details on its calculation), the explicit cartesian coordinates of the molecule selected as luminescent unit (high ONIOM layer) optimized to both ground and excited state and the optimized basis set, in Gaussian16 format, employed for the level of theory of the high ONIOM layer.

Optimized unit cell (atomic species, x/a, y/b, z/c)

```
Space group: Pna21, orthorhombic
Unit cell parameters
a=20.61033352, b=22.37987285, c=5.89586295
fractional coordinates
 S   -0.030037512    -0.041258907    -0.411473240
 S   -0.116690317    +0.060688614    -0.272803447
 O   -0.062876600    -0.126497628    +0.148442635
 N   +0.391255287    -0.252678770    -0.292840485
 N   +0.239625609    +0.361581470    +0.231967251
 N   -0.094420019    -0.041362067    -0.038196679
 C   +0.181904579    -0.391005951    +0.068822751
 C   +0.123404359    -0.364632899    +0.107896997
 C   +0.071415229    -0.393954872    +0.245751384
 C   +0.007726810    -0.397972845    +0.162606545
 C   +0.083394131    -0.413527570    +0.467883360
 C   -0.041901356    -0.421742942    +0.295066331
 C   +0.033878788    -0.437606189    -0.399439789
 C   -0.029148307    -0.441838972    -0.484860683
 C   +0.104682885    -0.305077262    +0.016795741
 C   +0.064321303    -0.267514159    +0.146171138
 C   +0.120569430    -0.286568408    -0.204901588
 C   +0.040241027    -0.214132653    +0.061537152
 C   +0.096254322    -0.233455436    -0.291175754
 C   +0.054727524    -0.196307101    -0.161977381
 C   +0.238794423    -0.357358980    -0.019106569
 C   +0.277263315    -0.378302775    -0.199419328
 C   +0.257005775    -0.302529612    +0.078311298
```

C	+0.327021340	-0.344349152	-0.292933053
C	+0.308418673	-0.269104728	-0.005808295
C	+0.343435848	-0.287887568	-0.199757052
C	+0.192717605	-0.455968109	+0.116106473
C	+0.217393273	-0.475623111	+0.324120279
C	+0.183431725	-0.499010834	-0.052931258
C	+0.231958008	+0.464799453	+0.365210254
C	+0.199285258	+0.441107171	-0.017010468
C	+0.223782044	+0.421339881	+0.193229700
C	+0.414476779	-0.199514620	-0.175928145
C	+0.415845601	-0.264349319	+0.480208669
C	+0.284875186	+0.349381957	+0.416534485
C	+0.244999080	+0.321576708	+0.038065826
C	+0.030565980	-0.142925774	-0.272994432
C	-0.014826294	-0.101456870	-0.216611754
C	-0.057542270	-0.094116113	-0.017118679
C	-0.084589184	-0.006628361	-0.224233798
C	-0.139675004	-0.023251879	+0.139145294
H	-0.002547610	-0.382546604	-0.007714772
H	+0.131538910	-0.408751709	-0.461117704
H	-0.090332657	-0.425466033	+0.224474181
H	+0.044408579	-0.452934532	-0.229072799
H	-0.067751599	-0.460928492	-0.382606531
H	+0.050850839	-0.281448627	+0.315785300
H	+0.151749510	-0.314311652	-0.308863578
H	+0.009001960	-0.186395785	+0.164129042
H	+0.109008798	-0.220013127	-0.462411951
H	+0.268110664	-0.422532529	-0.267506673
H	+0.229859945	-0.285743706	+0.222904021
H	+0.354437192	-0.362021199	-0.435097096
H	+0.320194909	-0.226864876	+0.073574316
H	+0.226964497	-0.442797231	+0.454853385
H	+0.164329575	-0.485898789	-0.217219920
H	+0.252364112	+0.452892703	-0.471783399
H	+0.192654569	+0.409773478	-0.154961306
H	+0.426598114	-0.209858364	+0.000368229
H	+0.458857253	-0.184468277	-0.259162288
H	+0.378751935	-0.163020028	-0.179713836
H	+0.433437487	-0.222387848	+0.407634912
H	+0.455676557	-0.296688778	+0.480515975
H	+0.377792531	-0.281914772	+0.369942768
H	+0.293280428	+0.301505489	+0.426164171
H	+0.331414704	+0.372205972	+0.392260652
H	+0.264424542	+0.363791625	-0.421653165
H	+0.253653127	+0.276431593	+0.100760076
H	+0.199524943	+0.320607524	-0.057541370
H	+0.284661926	+0.334493383	-0.077134753
H	+0.053375220	-0.134886560	-0.437267296
H	-0.183279526	-0.006274871	+0.058471721
H	-0.150287451	-0.062497570	+0.241351466
H	-0.118292743	+0.011819916	+0.244336539

Cartesian coordinates (atomic species, x,y,z in Å) **for high-layer molecular unit optimized at the excited state S_1**

S	4.58869800	-2.93519900	-5.37676800
S	6.99914600	-4.58484800	-4.58937500
O	2.74138800	-3.70483600	-2.06377400
N	-0.65963000	5.38446700	-4.69038900
N	-8.98480200	1.73100100	-1.44994500
N	4.67928100	-4.24431000	-3.20940200
C	-3.40997800	0.96455700	-2.46424500
C	-2.74522700	-0.20760500	-2.26938000
C	-3.34120700	-1.30952700	-1.48950000
C	-3.26090300	-2.62618700	-1.96389700
C	-3.84964200	-1.09099800	-0.20204400
C	-3.70356000	-3.68610100	-1.19043200
C	-4.27925300	-2.15507500	0.57887000
C	-4.21042200	-3.45721500	0.08986800
C	-1.40954800	-0.51167100	-2.83796000
C	-0.49424400	-1.25417500	-2.08384700
C	-1.05239600	-0.15382400	-4.14405100
C	0.72695800	-1.65148100	-2.60310700
C	0.16043800	-0.56688600	-4.67491800
C	1.06463100	-1.35424500	-3.93581000
C	-2.75639900	2.16981000	-3.00153200
C	-3.32078300	2.93248900	-4.04656300
C	-1.53128100	2.61801900	-2.46016300
C	-2.65121400	3.98622400	-4.62974000
C	-0.87737600	3.70728000	-2.97677600
C	-1.38846900	4.39381600	-4.11583500
C	-4.86759900	1.10038100	-2.19454500
C	-5.32496600	1.58175400	-0.96674200
C	-5.82191300	0.84306400	-3.18072100
C	-6.66796400	1.76531900	-0.69971800
C	-7.17305300	1.07035100	-2.95081100
C	-7.63127400	1.52334900	-1.70142600
C	0.51445100	5.95191000	-4.02473100
C	-0.97001700	5.92312100	-6.00509000
C	-9.29631200	2.69895500	-0.40255300
C	-9.88409300	1.79668700	-2.59242600

C	2.27581300	-1.78156700	-4.60111100
C	3.23501100	-2.69402300	-4.22961800
C	3.44356200	-3.54692000	-3.07860800
C	5.43395300	-4.00953300	-4.29200200
C	5.13458400	-5.15972000	-2.17804300
H	-2.85236300	-2.79457800	-2.94806100
H	-3.84365700	-0.09055600	0.20616000
H	-3.66202200	-4.68985800	-1.59731500
H	-4.66250500	-1.97682800	1.57495800
H	-4.55234600	-4.28668900	0.69941400
H	-0.77087500	-1.55262000	-1.07932000
H	-1.74075000	0.41800000	-4.75728300
H	1.41541200	-2.24475000	-2.01822300
H	0.42665600	-0.28344200	-5.68843500
H	-4.31201300	2.67211000	-4.39353800
H	-1.09682500	2.06438000	-1.63569200
H	-3.09981200	4.52830700	-5.45487400
H	0.07958700	4.00120700	-2.57198100
H	-4.58842400	1.84002000	-0.22148200
H	-5.51220200	0.46344500	-4.14792200
H	-6.95642500	2.16898900	0.26063900
H	-7.87551700	0.89829400	-3.75380900
H	0.27685900	6.20272700	-2.99114300
H	0.78459200	6.86851400	-4.54595500
H	1.35122300	5.25104900	-4.05946100
H	-0.02829400	6.12245400	-6.52284600
H	-1.52033100	6.85898300	-5.91163700
H	-1.56135300	5.23157600	-6.59568200
H	-10.37086800	2.82835900	-0.34790700
H	-8.82675600	3.66678200	-0.60411300
H	-8.94293000	2.34333400	0.56413900
H	-10.90192300	1.90181700	-2.22304200
H	-9.83895500	0.87198200	-3.17050100
H	-9.63929700	2.64442300	-3.24947600
H	2.44655900	-1.30493600	-5.56445900
H	5.60316500	-6.00913100	-2.66000000
H	4.26365500	-5.46100500	-1.60388700
H	5.86922900	-4.67354500	-1.53405000

Cartesian coordinates (atomic species, x,y,z in Å) **for high-layer molecular unit optimized at the ground state S_0**

S	4.56426200	-2.92532100	-5.39610500
S	6.95370200	-4.56830200	-4.60407600
O	2.75335300	-3.67810400	-2.06309600
N	-0.58381800	5.35079500	-4.74829000
N	-9.00576400	1.71279900	-1.43647200
N	4.66211900	-4.24269500	-3.20766700
C	-3.43337800	0.97795600	-2.50323600
C	-2.75542200	-0.17681600	-2.27906200
C	-3.32362200	-1.29010600	-1.47423100
C	-3.28342200	-2.60146200	-1.96256500
C	-3.79942500	-1.08061000	-0.17624400
C	-3.71928000	-3.66611300	-1.18759300
C	-4.24856800	-2.14386300	0.59734700
C	-4.20668400	-3.44330500	0.09961400
C	-1.41140300	-0.46166800	-2.82707700
C	-0.52435900	-1.24883500	-2.07536400
C	-1.02932300	-0.09979800	-4.13187600
C	0.68500600	-1.67626800	-2.58617600
C	0.16722100	-0.54761100	-4.65588300
C	1.04335500	-1.36316800	-3.90805700
C	-2.77102000	2.18903400	-3.02443000
C	-3.30181300	2.94019700	-4.08217800
C	-1.56027900	2.63078400	-2.47059200
C	-2.60412800	3.98524000	-4.66691500
C	-0.87805300	3.71017100	-2.99689600
C	-1.34688300	4.37737900	-4.15045900
C	-4.88752500	1.08936800	-2.21081500
C	-5.33724000	1.54646200	-0.97326100
C	-5.84323700	0.84897400	-3.19605100
C	-6.67984900	1.73305000	-0.70134400
C	-7.19531300	1.07347200	-2.95614200
C	-7.64657000	1.50752000	-1.70139300
C	0.54522500	5.93554500	-4.04072800
C	-0.97790200	5.93742500	-6.01156800
C	-9.29492600	2.70896700	-0.40912000
C	-9.89517300	1.80431400	-2.58437200
C	2.24554800	-1.79984100	-4.56919900
C	3.21730800	-2.68676600	-4.23527400
C	3.44443100	-3.54484300	-3.06402600
C	5.40936400	-3.99369700	-4.30611800
C	5.13565900	-5.16016900	-2.18039900
H	-2.90847600	-2.77175200	-2.96161500
H	-3.78144800	-0.08293100	0.23904300
H	-3.70129300	-4.66649900	-1.60696300
H	-4.62885400	-1.96414700	1.59473000
H	-4.55988500	-4.27213400	0.70426200
H	-0.82247200	-1.55023600	-1.07939500
H	-1.68753400	0.51907500	-4.72975500
H	1.35407900	-2.27811500	-1.99303800
H	0.45112800	-0.26400900	-5.66424800

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H  -4.29255400    2.69567700   -4.44566100
H  -1.15754700    2.10714200   -1.60839500
H  -3.03683500    4.52285900   -5.50487800
H   0.05898600    4.01584100   -2.55300700
H  -4.59826500    1.79933700   -0.22778700
H  -5.53763100    0.48847900   -4.17182800
H  -6.96323000    2.12784300    0.26448500
H  -7.89991600    0.91505100   -3.76034500
H   0.24097800    6.31384700   -3.06002400
H   0.91981800    6.77514400   -4.62543200
H   1.35134800    5.20593500   -3.91817000
H  -0.08634500    6.34113900   -6.49774400
H  -1.70740000    6.74092500   -5.88764700
H  -1.42423800    5.19420600   -6.67041900
H -10.36813600    2.84861300   -0.34304500
H  -8.81978700    3.66891500   -0.63796600
H  -8.93256200    2.37425900    0.56164500
H -10.91403200    1.92515900   -2.22132500
H  -9.86263200    0.88276300   -3.16870900
H  -9.63085100    2.65140300   -3.23615000
H   2.39685200   -1.32574300   -5.53929800
H   5.59113100   -6.01106500   -2.67108700
H   4.27568900   -5.46371200   -1.59188700
H   5.88018100   -4.67148200   -1.55124800
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Basis sets used for the high-layer calculations (Gaussian format)

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C       0
S   6  1.00
       3048.0   0.001826
       456.40   0.014060
       103.70   0.068760
       29.230   0.230400
       9.3490   0.468500
       3.1890   0.362800
SP  2  1.00
       3.6650   -0.3959 0.2365
       0.7705    1.2160 0.8606
SP  1  1.00
       0.212476292743   1.0     1.0
D   1  1.00
       0.831504369588   1.0
****
N       0
S       7       1.00
      7590.0    0.000889
      991.20    0.008994
      190.10    0.052870
      52.690    0.171000
      18.100    0.361200
      7.0480    0.402700
      2.9220    0.154900
SP      3       1.0
      18.40  -0.02807   0.01869
      4.242  -0.11460   0.10130
      1.347   0.18900   0.23940
SP      1       1.0
      0.468530523588    1.0     1.0
SP      1       1.0
      0.146242193840  1.0       1.0
D       1       1.0
        0.78199747455   1.0
****
O       0
S       8       1.0
        8020.0  0.00108
        1338.0  0.00804
        255.40  0.05324
        69.220  0.16810
        23.900  0.35810
        9.2640  0.38550
        3.8510  0.14680
        1.2120  0.07280
SP      4       1.0
        49.43  -0.00883 0.00958
        10.47  -0.09150 0.0696
        3.235  -0.04020 0.2065
        1.217   0.37900 0.347
SP      1       1.0
        0.478437802626  1.0     1.0
SP      1       1.0
        0.169516407504  1.0     1.0
D       1       1.0
        0.848511101135  1.0
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H       0
S       5       1.0
        153.80  0.0026
        31.821 -0.0028
        21.650  0.028
        3.4920  0.193
```

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        0.7890  0.791
S       1       1.0
        0.2364860243740 1.0
S       1       1.0
        0.0826357461193 1.0
P       1       1.0
        0.8432885490860 1.0
****
S       0
S       8       1.0
        109211.00       0.0002520
        16235.206       0.0019934
        3573.0286       0.0111177
        943.23811       0.0498945
        287.26179       0.1661455
        99.914226       0.3627018
        38.602137       0.4108787
        15.531224       0.1457875
SP      6       1.0
        281.22171      -0.0057780       0.0081427
        67.106575      -0.0665855       0.0565570
        21.794135      -0.1203552       0.2039582
        8.2097646       0.2741310       0.3973328
        3.4178289       0.6463829       0.3946313
        1.5452225       0.2925792       0.1544345
SP      3       1.0
        4.3752432      -0.1750000      -0.0613439
        1.8096201      -0.5938952       0.1272251
        0.6833985       0.8298996       1.2215893
SP      1       1.0
        0.2413  1.0     1.0
SP      1       1.0
        0.1060  1.0     1.0
D       1       1.0
        0.3830  1.0
```

Comment [FL]: Use same format as in main document.

References:

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