Supporting information

Excimer Formation and Evolution of Excited State Property in

Discrete Dimeric Stacking of Anthracene Derivative: A

Computational Investigation

Yu Gao,^{a‡} Haichao Liu,^{a‡} Shitong Zhang,^a Qiang Gu*^b, Yue Shen,^a Yunpeng Ge,^a Bing Yang*^a

^a State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China

^b College of Chemistry, Jilin University, Changchun, 130012, P. R. China

E-mail: <u>yangbing@jlu.edu.cn</u> E-mail: guq@jlu.edu.cn

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SI-1:Experimental details

In order to confirm the excimer formation, the concentration-dependent PL spectra of 2-TA-AN were examined in THF solutions. The PL intensities of 2-TA-AN in THF solutions with incremental concentrations are normalized at wavelength of 460 nm between the regions of former and latter fluorescence. An excimer-like emission band arises with a peak at 526 nm upon the concentration of 0.1 mol·L⁻¹, and the resolved excimer spectrum is obtained by subtraction of the spectrum of the low-concentration solution (4.00×10^{-6} mol/L) from that of the high-concentration solution (2.73×10^{-1} mol/L). The PL spectrum in high-concentration $(2.73 \times 10^{-1} \text{ mol/L})$ solution shows the identical emission peak with that of 2-TA-AN crystal which was prepared by crystallization from THF:methanol (3:1, v/v) mixture. 2-TA-AN excimer in solutions lies in a complex surroundings while 2-AN-AN dimer shows the disperse distribution in crystal. 2-TA-AN dimer forms the excimer upon the photoexcitation, which displays the identical emission peak to that in high-concentration solutions. Thus, we can study the properties of anthracene excimer in depth by virtue of the advantage of disperse anthracene stacking in crystal, which cannot be yet solved by using excimer in solutions, because dimer structure in crystal is definite. All the quantum yields in this manuscript refer to the absolute quantum yields which were measured using an integrating sphere apparatus. We have deducted the background error during this measurement.



Figure S1 Top view of 2-TA-AN dimer in crystal, yellow zone represents the overlap area. One benzene ring can be roughly divided into 3 parallelograms, and the overlap extent is about 5 parallelograms, so the overlap ratio is about 5/(3*3)=5/9.



Figure S2 Polarity dependent steady state spectrum of 2-TA-AN monomer. Dualfluorescene phenomenon appears in acetonitrile.

SI-2: Functional and Basis set Selection

Table S1 Functional dependence of the 3-dimensional displacements of dimer (S_0) and excimer (S_1), absorption energy (E_{ab}) and emission energy (E_{em}) of the 2-TA-AN dimer



Parameter	B3lyp-D3	Cam-B3lyp-D3	M06-2X	M06-2X-D3	PBE0-D3	Crystal	Other works ¹
a _{S0} (Å)		3.938	3.327	3.339		3.466	
b _{S0} (Å)		-0.927	1.063	1.022		0.804	
c _{S0} (Å)		1.559	1.408	1.413		1.261	
Eabs (eV)	2.8558	3.4781	3.4889	3.4870	3.0349	3.0	3.23
$a_{S1}(Å)$		3.250	3.156	3.165	3.287		3.15
$b_{S1}(\text{\AA})$		0.511	0.771	0.743	0.522		
$c_{S1}(Å)$		0	0	0	0		
E _{emi} (eV)	2.1600	2.2481	2.1574	2.1521	1.8928	2.36	2.28

Table S2 Basis set dependence of the 3-dimension displacements of dimer (S_0) and excimer (S_1) , absorption energy and emission energy of the 2-TA-AN dimer

Parameter	6-31g(d,p)	6-31+g(d,p)	6-311+g(d,p)	aug-cc-pvdz	Crystal
$a_{S0}(Å)$	3.327	3.345	3.341	3.345	3.466
$b_{S0}(\text{\AA})$	1.063	1.131	1.088	1.088	0.804
$c_{S0}(\text{\AA})$	1.408	1.399	1.404	1.387	1.261
E _{abs} (eV)	3.4889	3.4298	3.4166	3.3714	3.0
$a_{S1}(Å)$	3.156	3.176	3.166		
$b_{S1}(\text{\AA})$	0.771	0.773	0.771		
$c_{S1}(Å)$	0	0	0		
E _{emi} (eV)	2.1574	2.1272	2.0976		2.36

SI-3: Optimized geometry and UV wavelengths of monomer, dimer and excimer,

accompanied with \mathbf{S}_1 state NTO of monomer.

Table S3 Calculated and experimental absorption and emission wavelengths of monomer and dimer.

Geometry	Absorption (nm)	Emission (nm)	
Monomer (experimental)	384,364,347,330	404, 424	
Monomer (calculated)	342.6	417.6	
Crystal (experimental)	413.3	526	
Dimer (crystal geometry)	353.8		
Dimer (optimized geometry)	355.4	574.7	



Figure S3 Ground state and excited state (S_1 state) gemoetry of 2-TA-AN and frontier molecular orbitals respectively



Figure S4 NTO of S_1 state based on S_1 optimized geometry of 2-TA-AN

Table S5 Frontier molecular orbitals and 3-dimensional displacements of ground state and \mathbf{S}_1 state of dimer

Geometry	НОМО	LUMO	Parameter (Å)
Crystal			a = 3.446 b = 0.804 c = 1.261



SI-4:NTOs and electron-hole pair of S₁ states of some certain points on the

potential energy surfaces of excimer



Figure S5 Atom lables in dimer system. We order the atoms from one monomer to the other by labeling anthracene moiety first and then thianthrene moiety. Since hydrogen atoms usually have little contribution to the transitions we are interested in, they are labled at the latest and usually ignored by default in TDM calculations.



Figure S6. Example of electron-hole pair. The transition density matrix can be outputted in the form of expansion by atomic-center basis functions in Gaussian09. The Mutiwfn can further contract such matrix to make it represented by atom centers. In this color-filled map, the brighter dot represents the higher value of matrix element. Diagonal terms, e.g. (1, 1), represents the magnitude of induced charge on atom 1 when the system undergoes electron transition process. While off-diagonal terms, e.g. (1, 29), displays the strength of electron-hole coherence between atom 1 and 29 when electron transits (detailed method see Chapter 3.21.2, Manual of Multiwfn 3.3.8.). According to our labeling method, atom 1 to 28 represent one monomer and atom 29 to 56 represent another monomer, and the map can be divided into four parts as Figure S4 shows. Two diagnoal parts are the LE transition of two monomers, off-diagonal parts are the CT transition from one monomer to another. So the contents of these two components in certain transition process can be evaluate according to the matrix elements.We evaluate the contents of them by using the equations below:

$$R_{LE} = \frac{M_{LE}}{M_{LE} + M_{CT}}$$
$$R_{CT} = \frac{M_{CT}}{M_{LE} + M_{CT}}$$

In equations, R_{LE} , R_{CT} represent the ratios of LE and CT in certain excited state, M_{LE} , M_{CT} represent the sum of the matrix elements in LE and CT areas respectively.



Figure S7 NTOs and electron-hole pair of S_1 state with variable distance along b-axis



Figure S8 NTOs and electron-hole pair of S1 state with variable distance along c-axis



Figure S9 NTOs of first five singlet excited state based on S_1 state geometry (3.12 Å vertical distance between two anthracence)



Figure S10 NTOs of first five singlet excited state based on S_1 state geometry (5.12 Å vertical distance between two anthracence). S_3 state is a pure CT state.

SI-5:The structure-property relationship of anthracene excimer in recent

literatures

Table S6 Interplanar distances and emission wavelengths of various anthracene excimer crystals in recent works

tag	interplanar distance/Å	λ_{em}/nm	literatures
tBuA	3.73	571	2
	3.33	570	3
∕~~ _{Br}	3.32	564	3
\rightarrow	3.40	554	3
Ļ	3.32	546	3
\mathbb{A}_{0}	3.30	544	3
o	3.40	537	3
-CN	3.32	537	3
13G	3.51	521	4
1a	3.45	515	5
3 a	3.48	505	5
2	3.43	501	4
10	3.46	500	4
1	3.55	494	4
3	3.53	494	4
11	3.40	479	4
14	3.43	475	4
no guest	3.25/3.34	473	3
15	3.34	468	4
13B	3.40	466	4
4a	3.45	465	5
12	3.32	463	4
CI	3.44	452	3
nPrA	3.30	452	2
2b	3.44	448	5
2a	3.40	447	5
EtA	3.54/3.57	442	2
nBuA	3.36	442	2
iso PrA(β)	3.87	420	2
iso PrA(a)	3.32		2



Figure S11 Correlations between interplanar distance of anthracene pair and emission wavelength of crystal in recent works. It is obvious that there is no significant relationship between interplanar distance and emission wavelengths.



Figure S12 Top view and side view of crystal packing mode of a) crystal 2, b) crystal 10 and c) crystal 13G in Reference 6d

SI-6: State composition of S1 state of each point on the potential energy surfaces

and correlations between overlap extent and emission wavelengths

Table S7 Content of CT in excimer along with different π - π distance (the displacements along band c-axis are kept constant, with 0.77 Å and 0 Å respectively)

π - π distance	Content of CT
3.15	0.446
3.25	0.435
3.35	0.422
3.45	0.404
3.55	0.382
3.65	0.358
3.75	0.329
3.85	0.293
3.95	0.253
4.05	0.21
4.15	0.168
4.25	0.13
4.35	0.096
4.45	0.069
4.55	0.049
4.65	0.034
5.15	0.047
5.65	1E-3

b-axis displacement	Content of CT	Overlap extent
0.77	0.446	0.638
0.87	0.444	0.591
0.97	0.441	0.544
1.07	0.438	0.497
1.17	0.433	0.450
1.27	0.428	0.403
1.37	0.419	0.356
1.47	0.409	0.302
1.57	0.398	0.259
1.67	0.385	0.219
1.77	0.369	0.183
1.87	0.311	0.149
1.97	0.396	0.120
2.07	0.395	0.093
2.17	0.390	0.070
2.27	0.383	0.050
2.37	0.374	0.034
2.47	0.367	0.020
2.57	0.361	0.010
2.67	0.354	0.004
2.77	0.348	4.16E-4
2.87	0.342	0
2.97	0.336	0
3.07	0.332	0
3.17	0.327	0
3.27	0.322	0
3.37	0.315	0
3.47	0.306	0
3.57	0.297	0
3.67	0.288	0
3.77	0.256	0
4.27	0.123	0
4.77	0.050	0
5.27	0.020	0
5.77	0.013	0

Table S8 Content of CT and overlap extent in excimer along with different b-axis dsiplacement (the displacements along π - π distance and c-axis are kept constant, with 3.15 Å and 0 Å respectively)

c-axis displacement	Content of CT	Overlap extent
0	0.446	0.638
0.1	0.445	0.633
0.2	0.444	0.628
0.3	0.443	0.628
0.4	0.441	0.615
0.5	0.440	0.607
0.6	0.436	0.599
0.7	0.432	0.590
0.8	0.427	0.580
0.9	0.418	0.570
1	0.406	0.559
1.1	0.388	0.547
1.3	0.228	0.521
1.4	0.250	0.509
1.5	0.271	0.498
1.6	0.407	0.487
1.7	0.417	0.477
1.8	0.423	0.467
1.9	0.427	0.459
2	0.430	0.451
2.1	0.431	0.444
2.2	0.431	0.437
2.3	0.431	0.432
2.4	0.429	0.427
2.5	0.427	0.423
2.6	0.424	0.417
2.7	0.420	0.412
2.8	0.414	0.405
2.9	0.407	0.398
3	0.398	0.390
3.2	0.370	0.372
3.6	0.374	0.327
3.8	0.370	0.301
4	0.360	0.278
4.2	0.342	0.258
4.6	0.158	0.227
4.8	0.120	0.216
5	0.090	0.207
5.5	0.048	0.172
6	0.073	0.119

Table S9 Content of CT and overlap extent in excimer along with different c-axis dsiplacement (the displacements along π - π distance and b-axis are kept constant, with 3.15 Å and 0.77 Å respectively)



Overlap extent

Figure S13 Correlations between π - π overlap extent of anthracene pair and emission wavelength of S₁ state and S₂ state.

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