Supporting Information

Intermolecular proton-coupled electron transfer reconstructs aggregates for near-infrared light-driven hydrogen evolution

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Content：

MD simulation and DFT calculation

Supplementary references

MD simulation: MD simulations were performed using the Amber 18 and GROMACS 4.6.7 packages[1] with amber gaff force field for AT molecules[2] and amber14SB force field for the explicit TIP3P.[3] The simulation parameters of AT molecule were derived from Gaussian 09 with B3LYP/6-31G* level. During the MD simulations, we used the SHAKE[4] method to restrict bonds, including H-bonding. During system modeling, the solute molecules were added into a cubic box of $5 \times 5 \times 5$ nm^3, and then the solvent molecules were used to fill the box.[5] The particle mesh Ewald summation method was used to describe long-range electrostatics.[6] The cutoff distance is 1.0 nm for nonbonded interactions. The Langevin thermostat and Berendsen barostat were used for temperature and pressure control. In the current study, a 200 ns MD trajectory was collected in each system. After the equilibration checking, only the final equilibrated 50 ns trajectory was used for further analysis.

DFT calculation: All calculations were completed by Gaussian 09 software. Density functional theory (DFT) was used to optimize the geometric structures on ground-state properties of AT and reconstructed AT with the B3LYP functional method in combination with the 6-31G* basis set,[7] while time-dependent DFT (TD-DFT, the same calculation method and basis set) was used to calculate the excited-state properties of AT and reconstructed AT aggregates. The convergence accuracy of SCF reached the default convergence standard. At the same time, the geometric configuration, HOMO-LUMO energy gap and excited-state orbital distribution of AT and reconstructed AT aggregates were analyzed and studied. The electrostatic potential and isosurface maps of various orbitals were exported and visualized with Multiwfn 3.8[8] and VMD
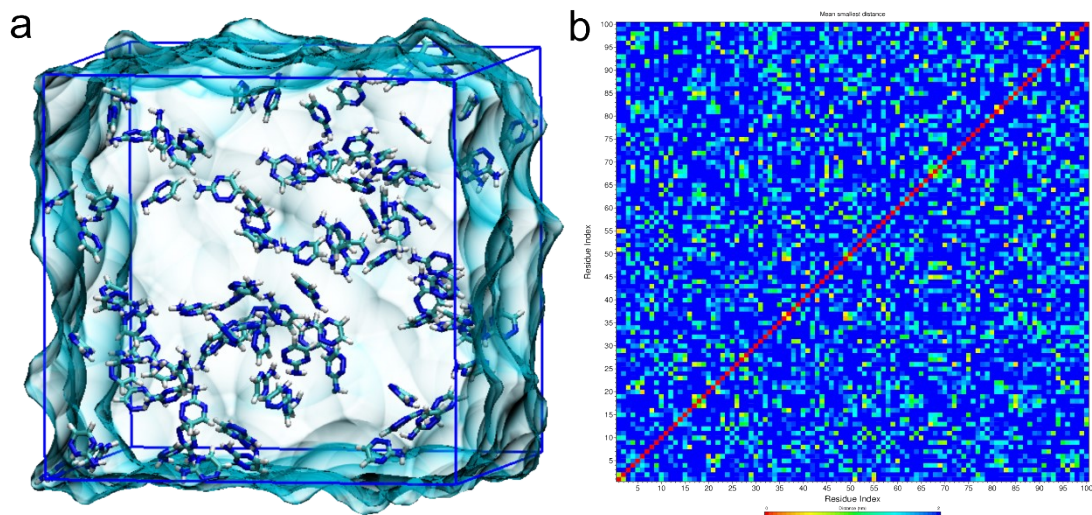
1.9.3 software.[9]
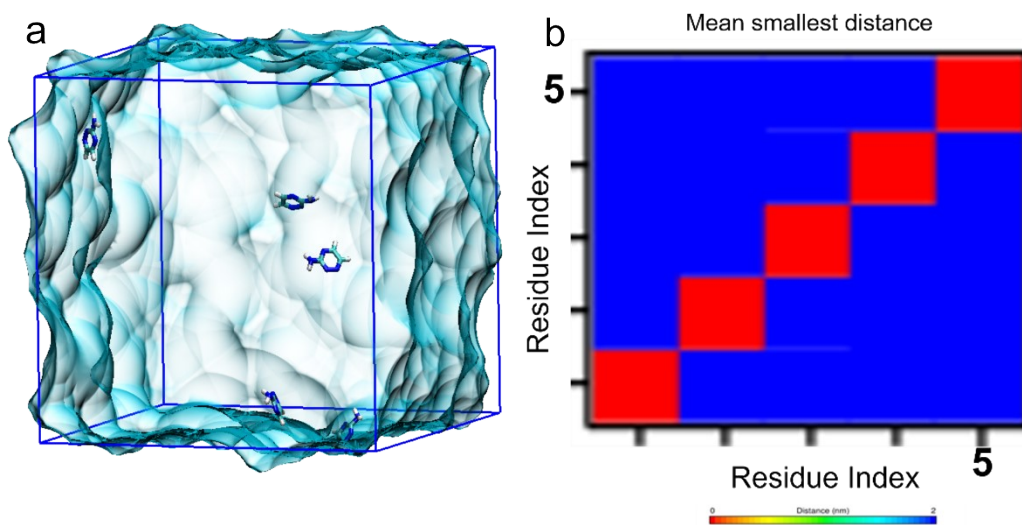
Fig. S1. (a) MD simulation of AT monomer, (b) AT monomer contact map based on MD simulations.
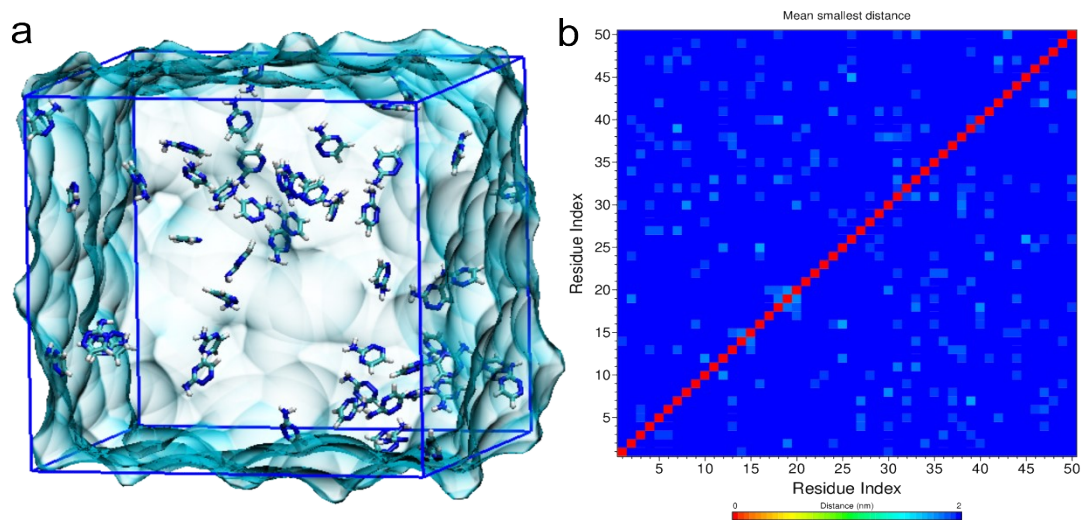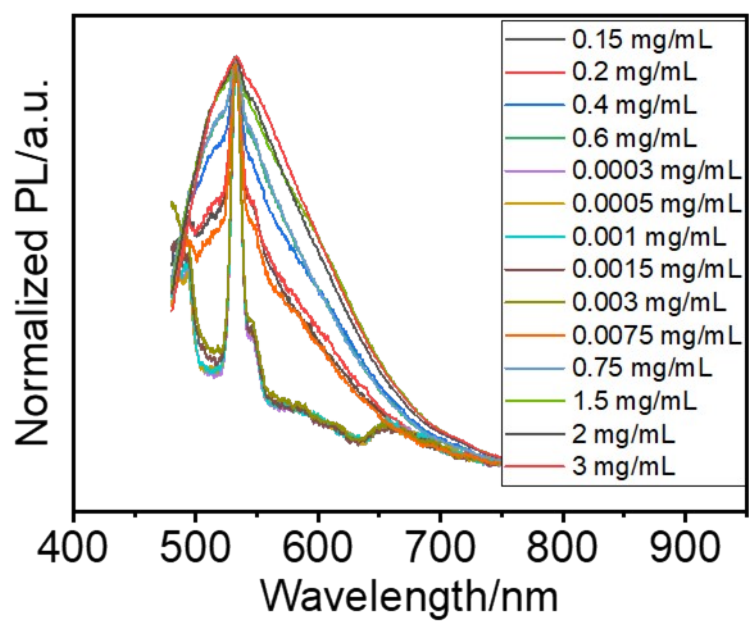
Fig. S2. (a) MD simulation of low aggregated AT, (b) Low aggregated AT contact map based on MD simulations.
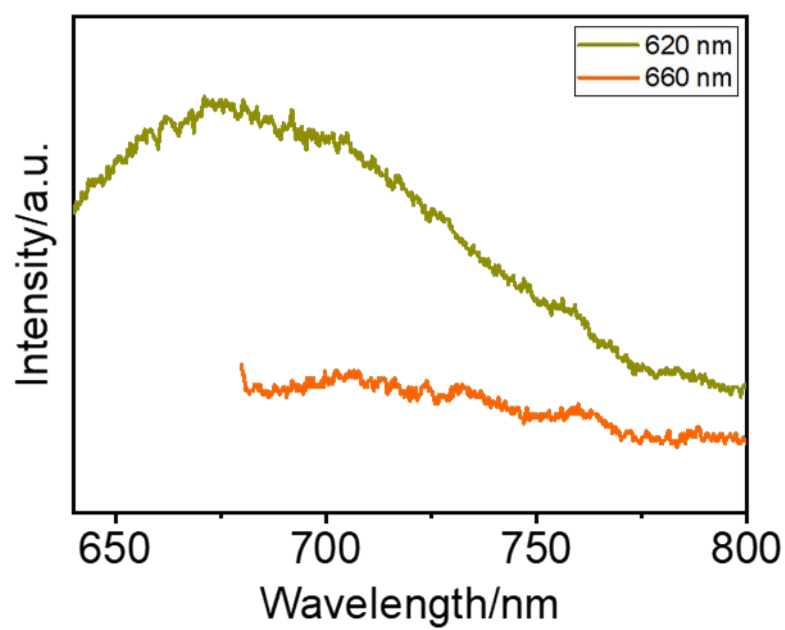
Fig. S3. (a) MD simulation of high aggregated AT, (b) High aggregated AT contact map based on MD simulations.

Fig. S4. Normalized PL spectra of AT with different concentrations.

Fig. S5. PL spectra of AT aggregates under long-wavelength excitation.
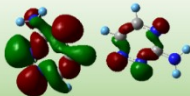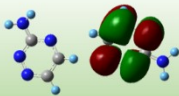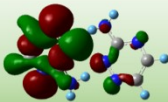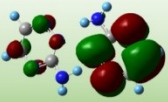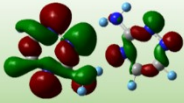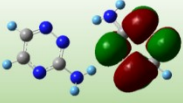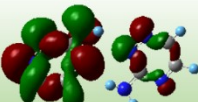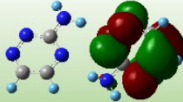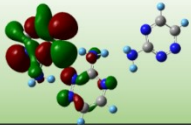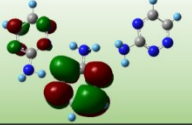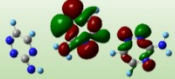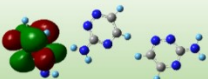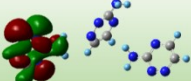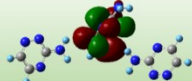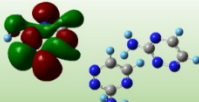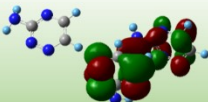
	HOMO	LUMO	Eg
Dimer			4.29 eV
Dimer			4.22 eV
Dimer			4.12 eV
Dimer			3.95 eV

Fig. S6. Calculated HOMO-LUMO gaps of AT dimers.

2	HOMO	LUMO	Eg
Trimer			4.24 eV
Trimer			4.13 eV
Trimer			4.09 eV
Trimer			3.96 eV

Fig. S7. Calculated HOMO-LUMO gaps of AT trimers.

2	HOMO	LUMO	Eg
Tetramer			3.92 eV
Tetramer			3.53 eV
Tetramer			3.38 eV
Tetramer			3.05 eV

Fig. S8. Calculated HOMO-LUMO gaps of AT tetramers.
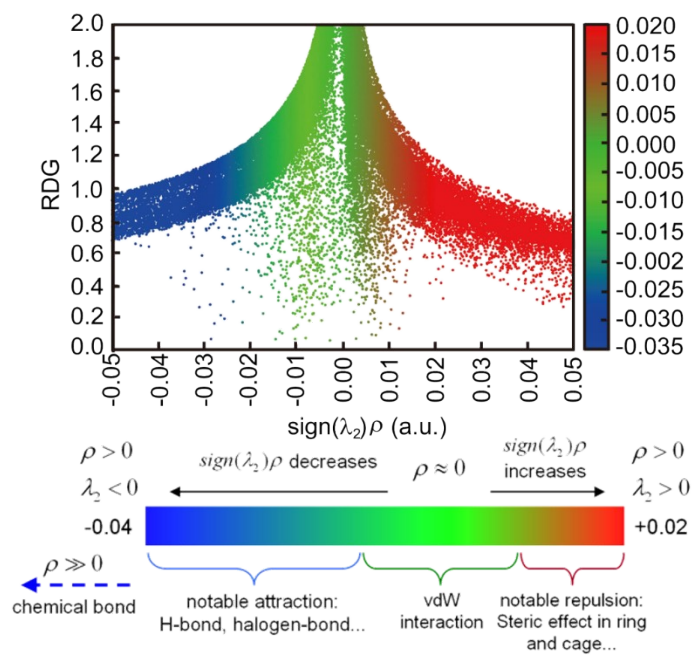
Fig. S9. The function of reduced density gradient and sign(λ_2)ρ scatter spectrum for AT aggregates based on a MD simulation.
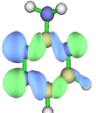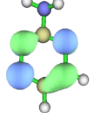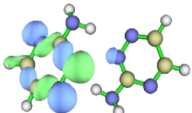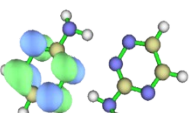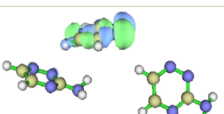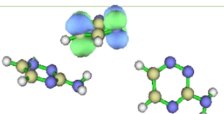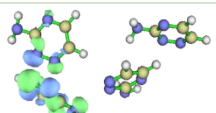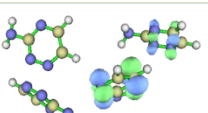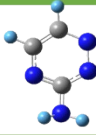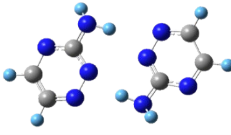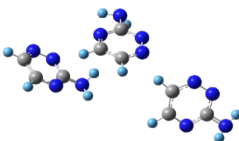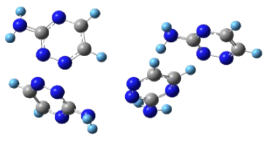
	HOMO	LUMO	Transition type
Monomer			$n \longrightarrow \pi^*$
Dimer			$n \longrightarrow \pi^*$
Trimer			$n \longrightarrow \pi^*$
Tetramer			$n \longrightarrow \pi^*$

Fig. S10. NTO orbital analysis of AT monomer and aggregates.

overlapping

allowed electronic transition
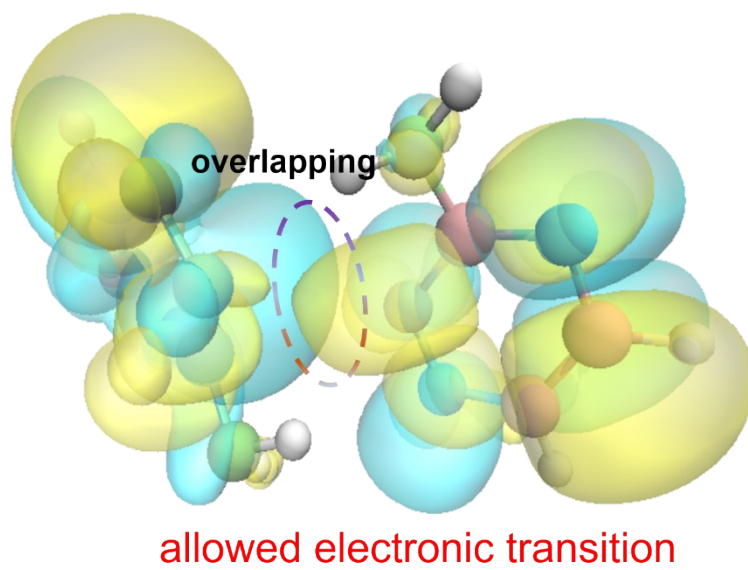
Fig. S11. Schematic diagram of n→π* electronic transition of a AT dimer aggregate.

Asymmetric structure		*f* (oscillator)
n=1		0.0054
n=2		0.0099
n=3		0.0103
n=4		0.0206

Fig. S12. Oscillator strengths of AT monomer and aggregates.
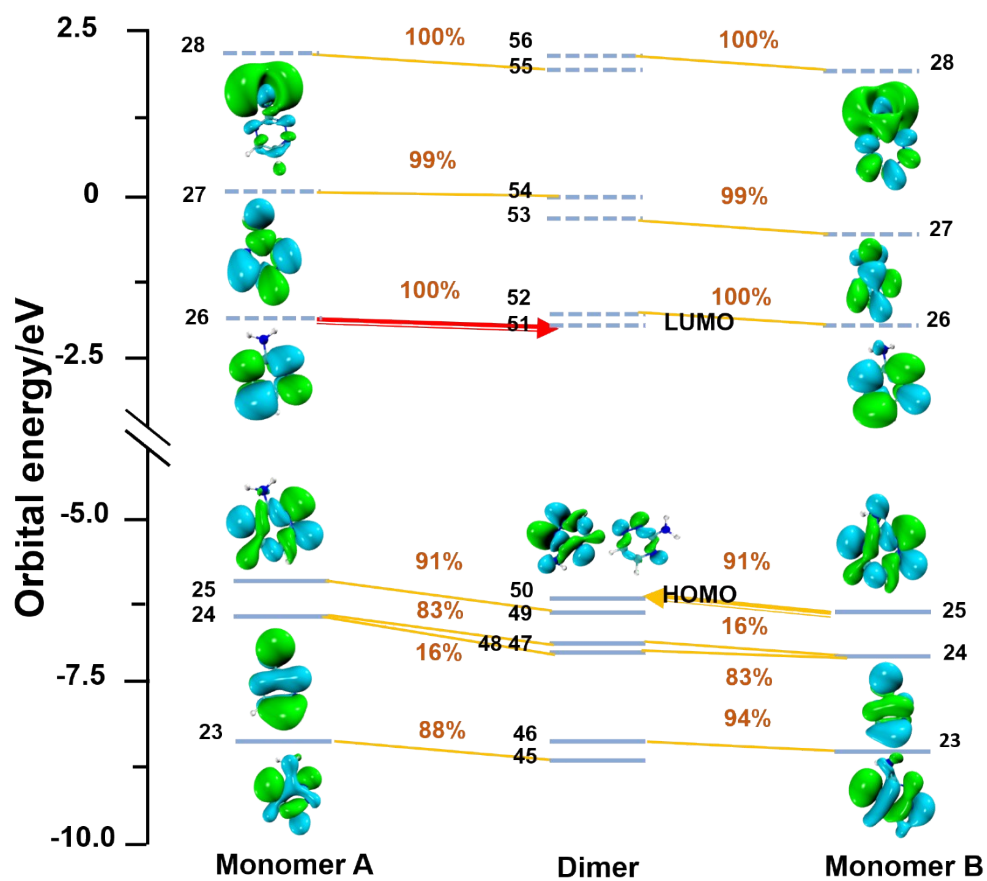
Fig. S13. Orbital interaction diagram of a AT dimer aggregate.
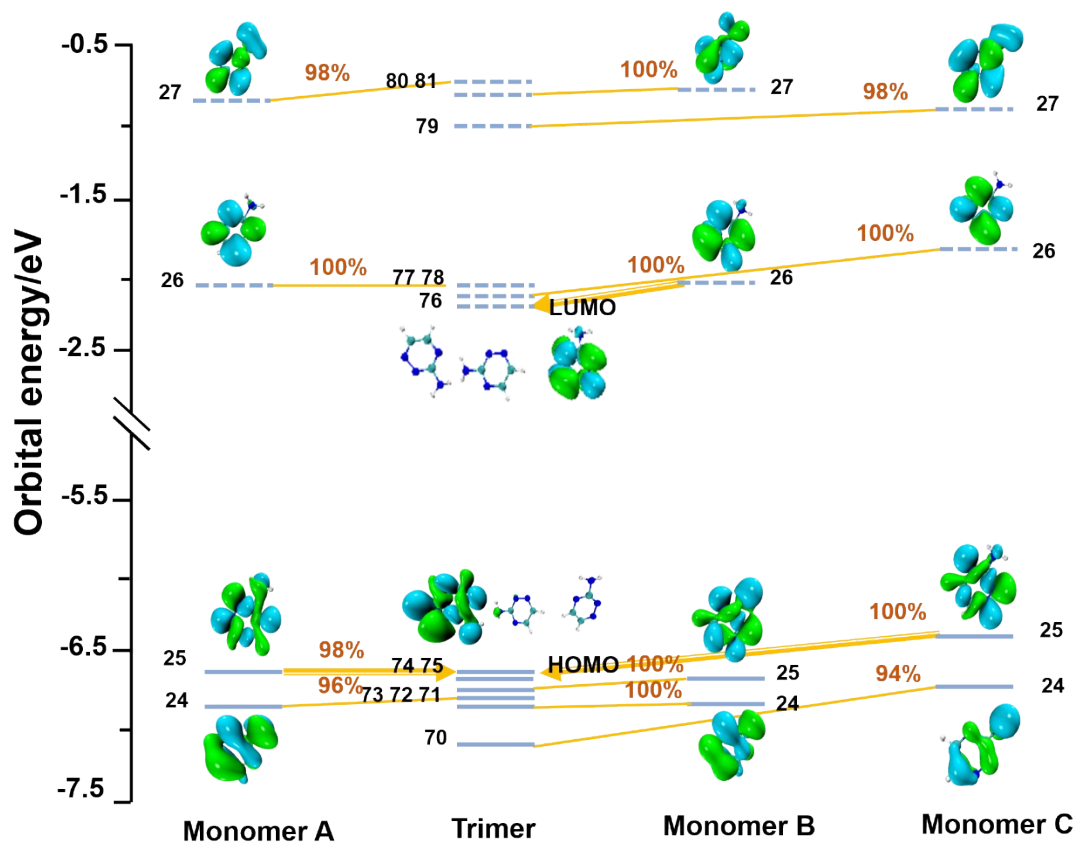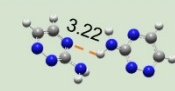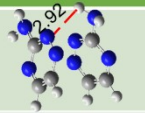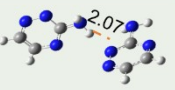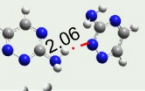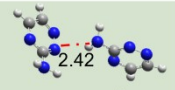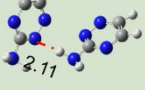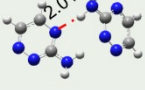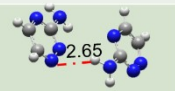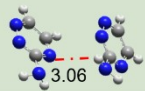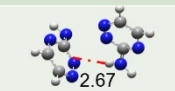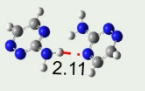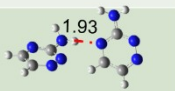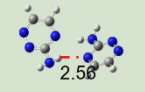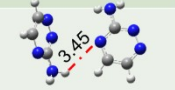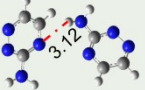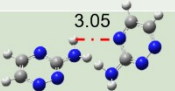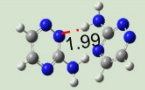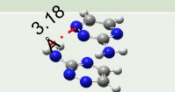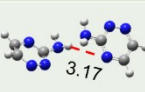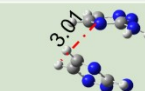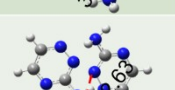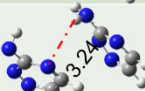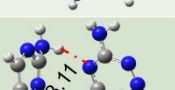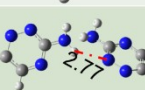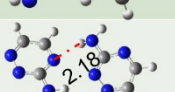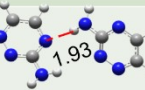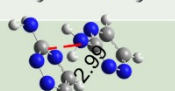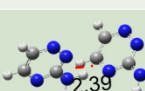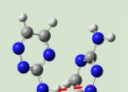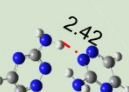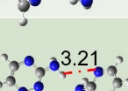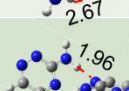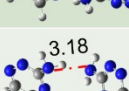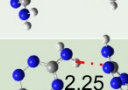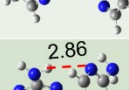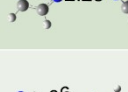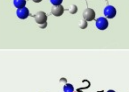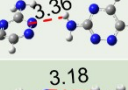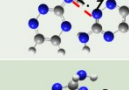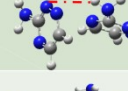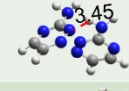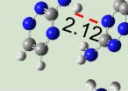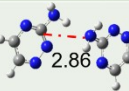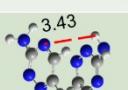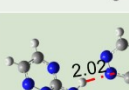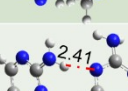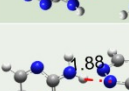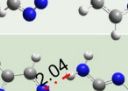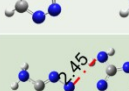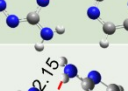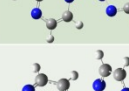
Fig. S14. Orbital interaction diagram of a AT trimer aggregate.

Atomic number	Distance (Å)	Atomic number	Distance (Å)
3-25	3.22	8-97	2.92
7-31	2.07	3-98	2.06
12-68	2.42	23-100	2.11
9-72	2.62	9-88	2.01
33-93	2.65	46-77	3.06
48-100	2.67	77-99	2.11
52-53	1.93	84-15	2.56
59-100	3.45	86-85	3.12
61-58	3.05	90-97	1.99
73-8	3.18	99-46	3.17
58-86	3.11	49-37	3.01
2-29	2.63	26-72	3.24
73-66	3.11	33-80	2.77
69-4	2.18	7-69	1.93
44-18	2.99	47-25	2.39

Atomic number	Distance (Å)	Atomic number	Distance (Å)
14-50		47-81	2.42
33-93	2.65Å 3.48	48-100	2.67
34-9	3.21	53-2	1.96
34-38	3.4	62-81	3.18
37-50	2.25	66-68	2.86
66-86	3.36	91-15	2.1
72-9	3.18	97-19	2.9
69-68	3.19	93-18	3.45
77-99	2.12	97-39	2.28
84-57	2.11	99-11	2.86
61-78	3.43	41-77	2.02
85-53	2.41	100-94	1.88
47-71	2.04	84-87	2.45
60-5	2.15	31-57	2.42
64-93	2.18	40-43	3.25

Fig. S15. Distance between adjacent AT molecules (b, c) based on MD simulation (a).
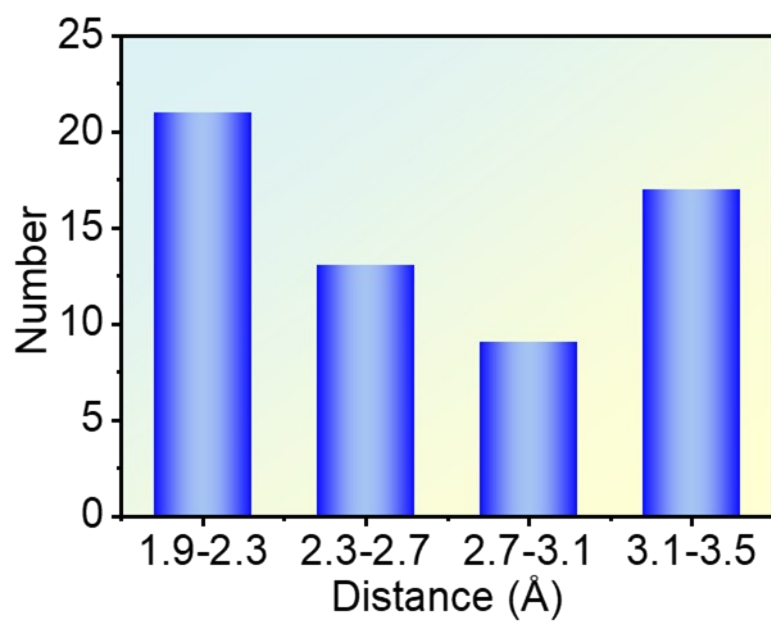
Fig. S16. Distance distributions between adjacent AT molecules based on S15.
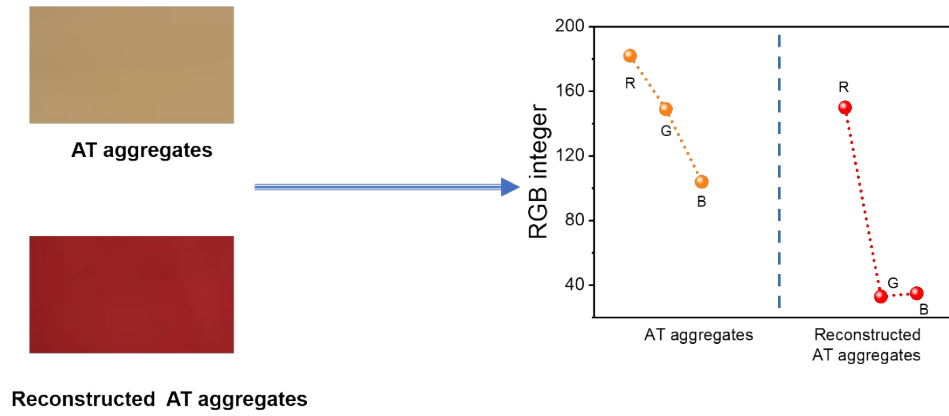
Fig. S17. RGB integer of AT aggregates and reconstructed AT aggregates (RGB represents the color of the red, green, and blue channels).

LUMO: -2.11 eV

LUMO: -3.20 eV

HOMO: -4.86 eV

HOMO: -6.37 eV

Eg=4.26 eV

AT aggregates

Eg=1.66 eV

**Reconstructed
AT aggregates**
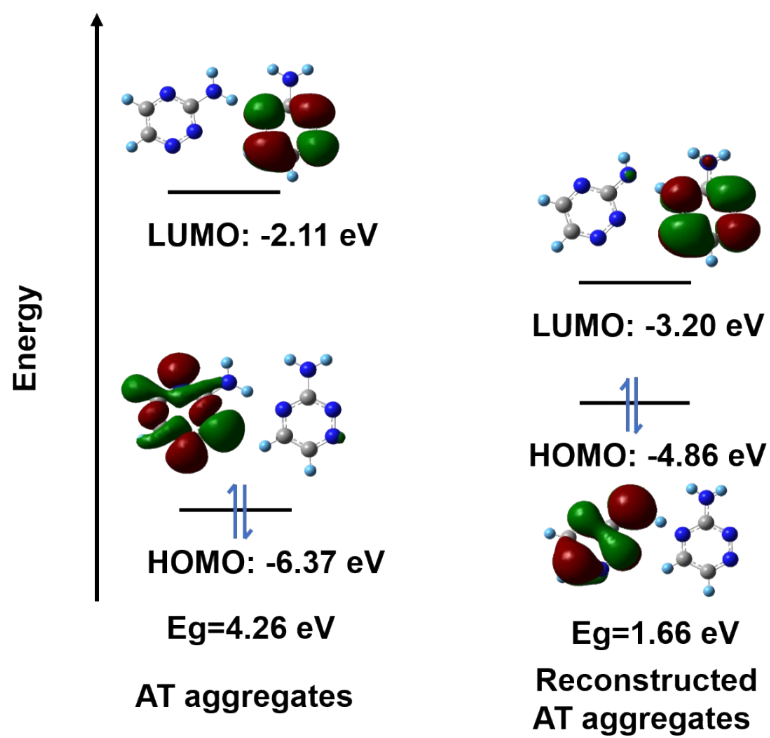
Fig. S18. Calculated HOMO-LUMO gaps of AT aggregates and reconstructed AT aggregates.
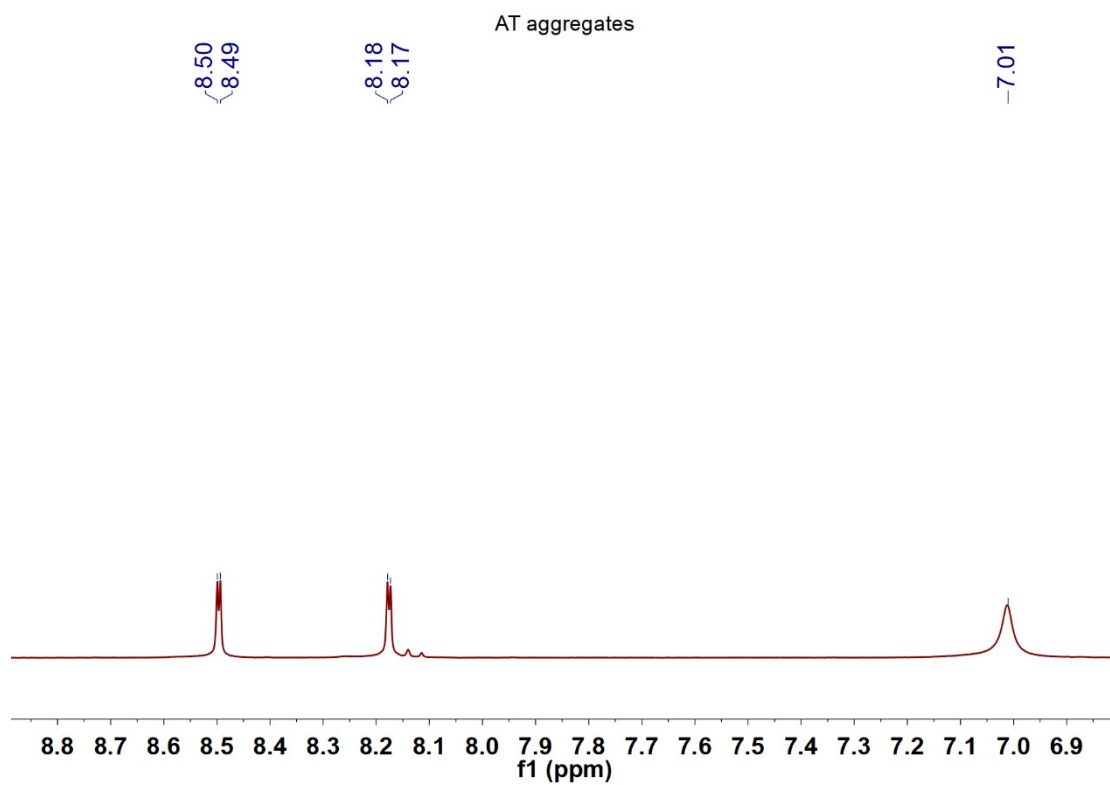
Fig. S19. ^{1}H-NMR spectra (in DMSO-d$_6$) of AT aggregates.
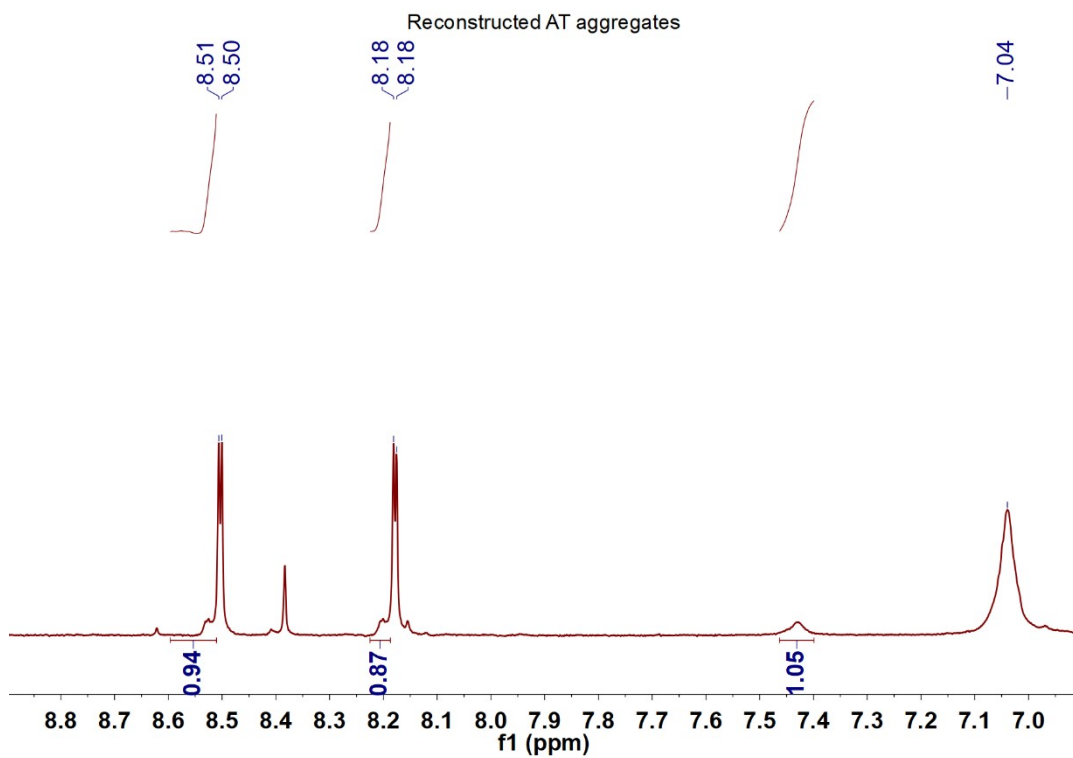
Fig. S20. ^{1}H-NMR spectra (in DMSO-d$_6$) of reconstructed AT aggregates.
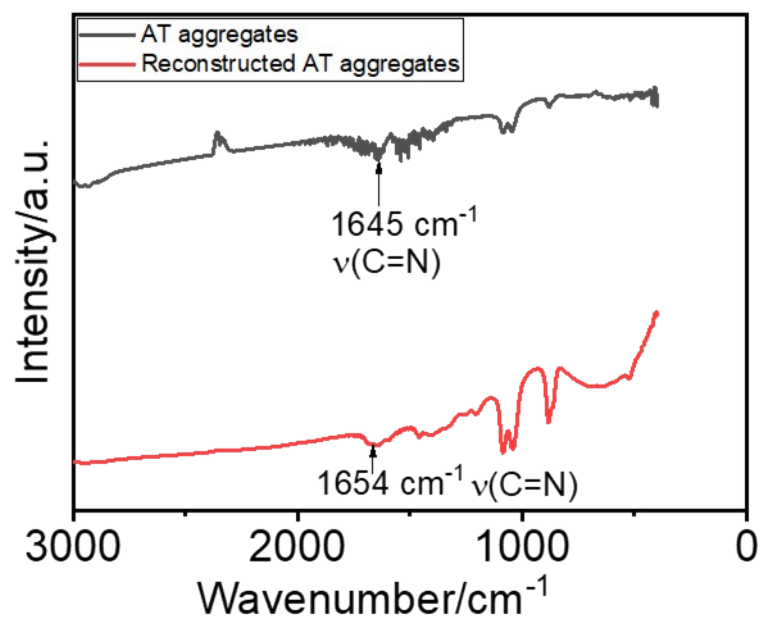
Fig. S21. FTIR spectra of AT aggregates and reconstructed AT aggregates.
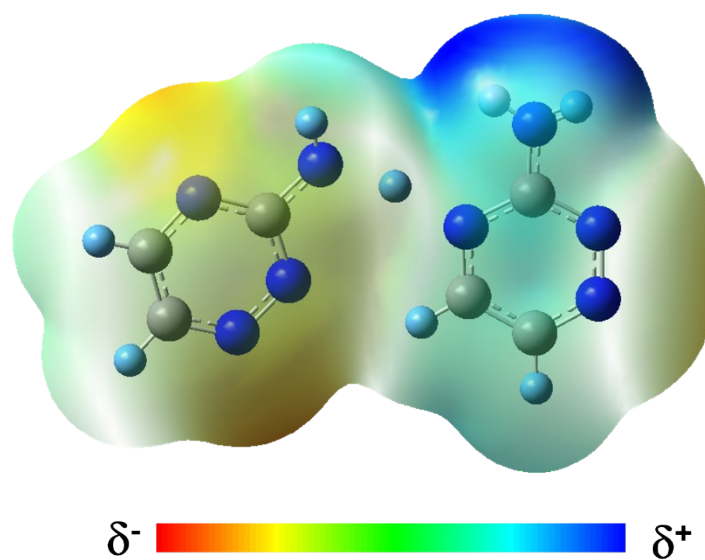
Fig. S22. Electrostatic potential distribution for reconstructed AT aggregates.

AT aggregates　　　**Reconstructed AT aggregates**

Coulomb attractive energy:6.69 eV　　Coulomb attractive energy: 3.15 eV

Coulomb attractive energy:5.94 eV　　Coulomb attractive energy: 4.55 eV

Coulomb attractive energy:5.17 eV　　Coulomb attractive energy: 3.83 eV

Coulomb attractive energy:4.66 eV　　Coulomb attractive energy: 4.42 eV
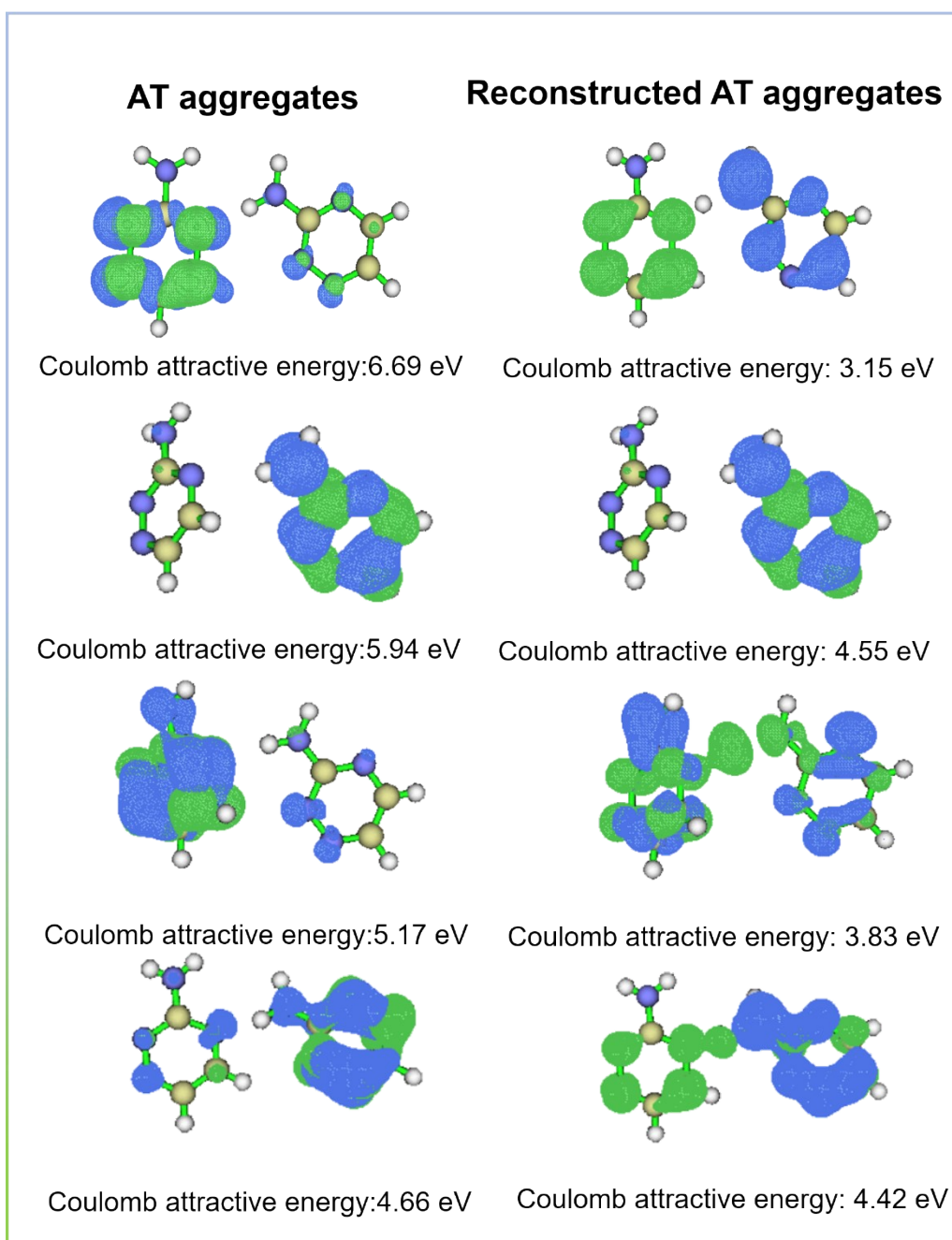
Fig. S23. Exciton binding energies of AT aggregates and reconstructed AT aggregates.
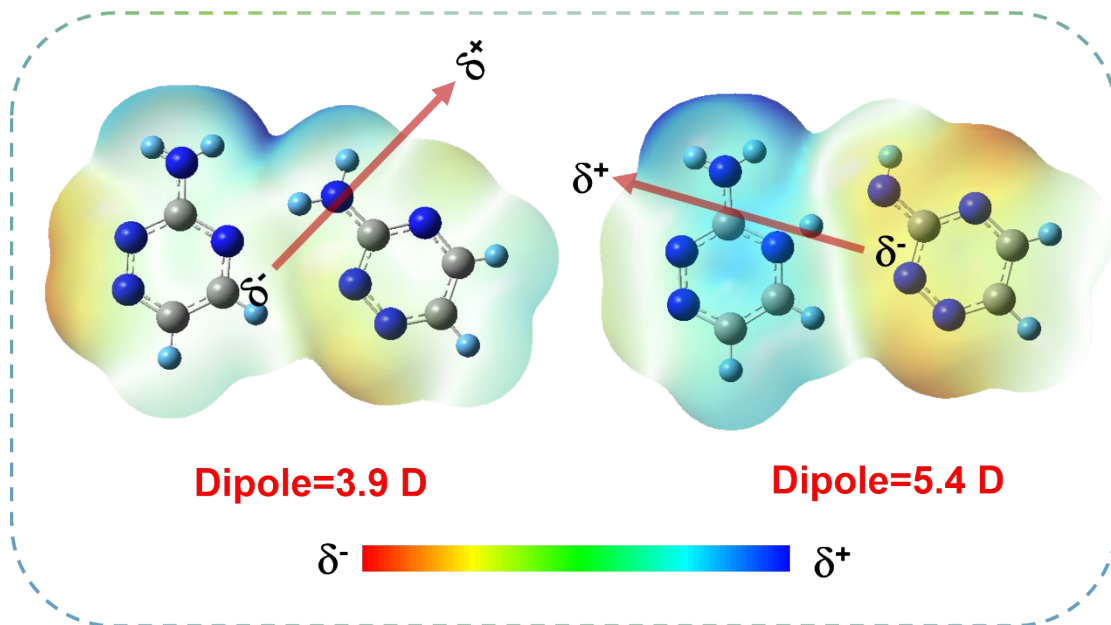
Fig. S24. Distribution of electrostatic potential and calculated dipole moments for AT aggregates and reconstructed AT aggregates.

	D (Å)	S_r (a.u.)	S_m (a.u.)	H (Å)	HDI	EDI
AT aggregates	0.506	0.745	0.526	2.192	9.30	9.41
Reconstructed AT aggregates	0.591	0.686	0.470	3.334	7.06	6.75

Fig. S25. Hole-electron analysis of AT aggregates and reconstructed AT aggregates.
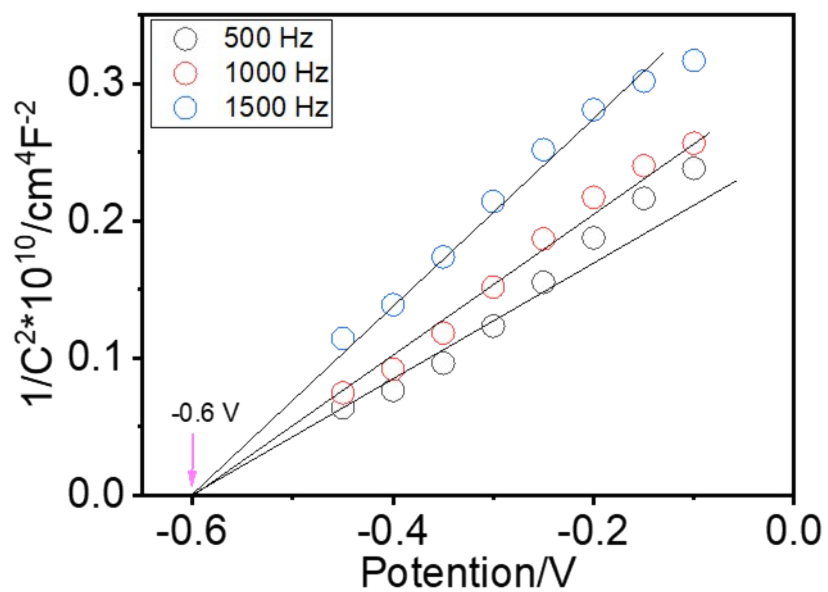
Fig. S26. Mott-Schottky plot of reconstructed AT aggregates. (As a rule of thumb, the difference between the CB and the FB is ~0.2 V[10]. The conduction band (CB) of reconstructed AT aggregates are estimated to be -0.56 V (vs NHE pH = 7)).
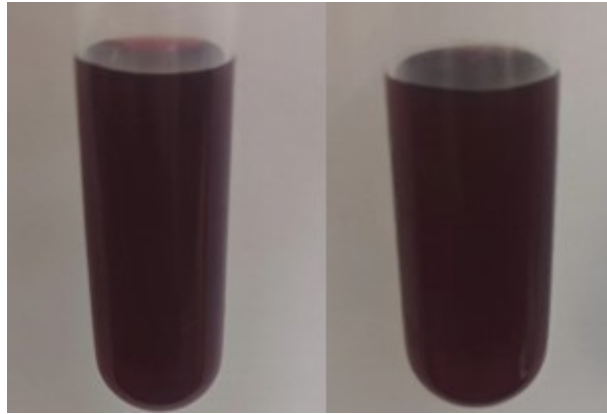
Fig. S27. The color change of the reconstructed AT aggregates after 48 hours test.
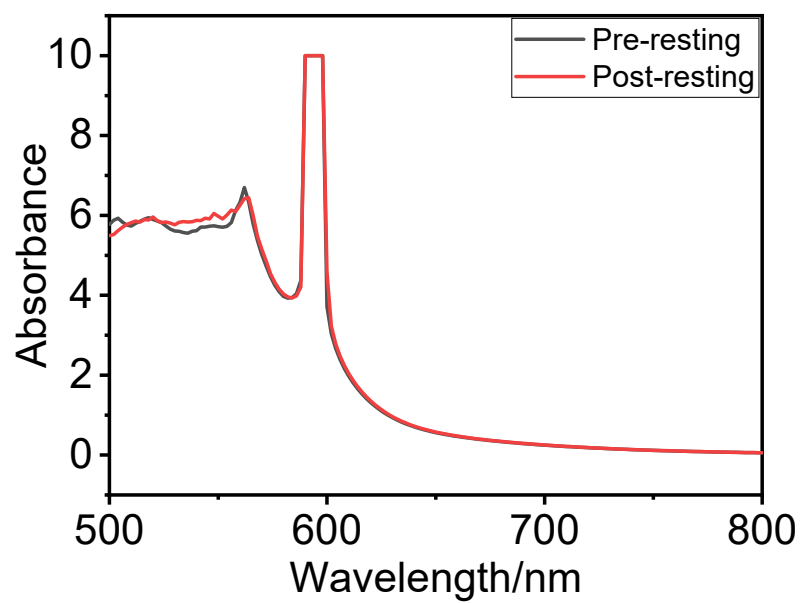
Fig. S28. UV-vis absorption spectra of the reconstructed AT aggregates after 48 hours test.
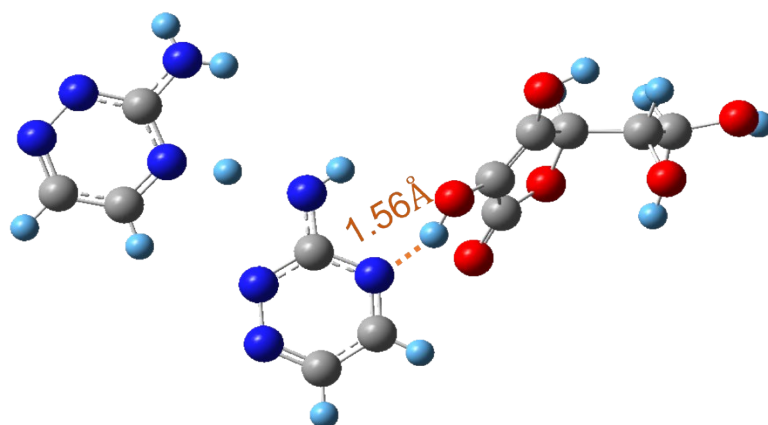
Interaction energy = -8.45 kJ/mol

Fig. S29. Hydrogen-bonded interactions between the reconstructed AT aggregates and L-A.
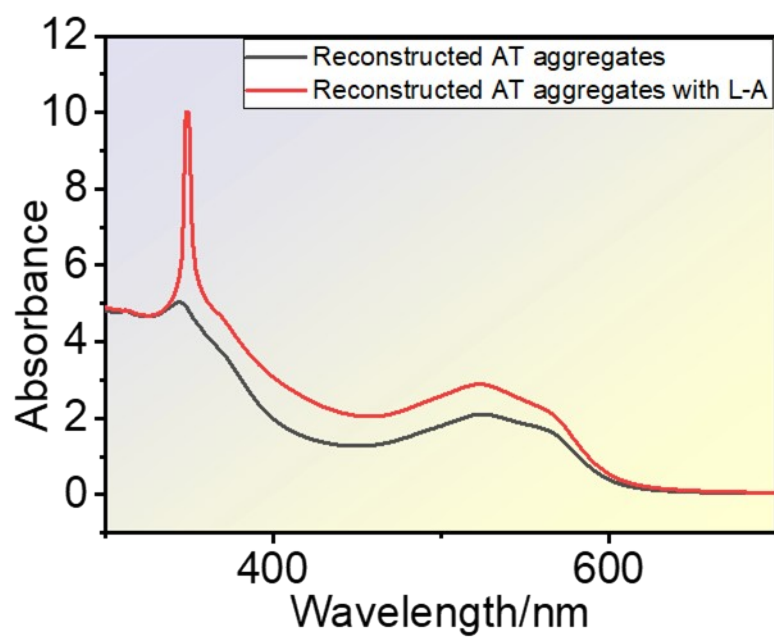
Fig. S30. UV-vis absorption spectra of reconstructed AT aggregates and reconstructed AT aggregates with L-A.
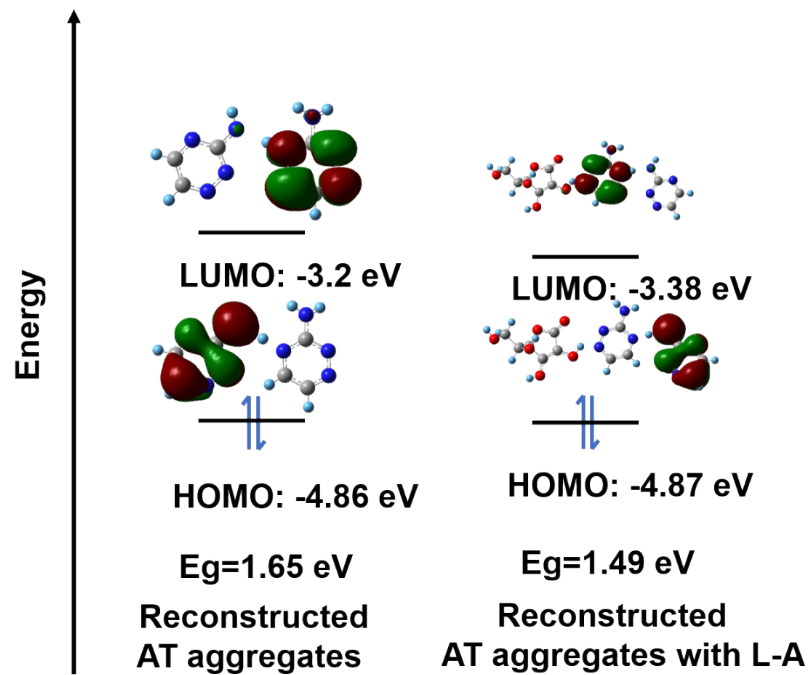
Fig. S31. Calculated HOMO-LUMO gaps of reconstructed AT aggregates and reconstructed AT aggregates with L-A.
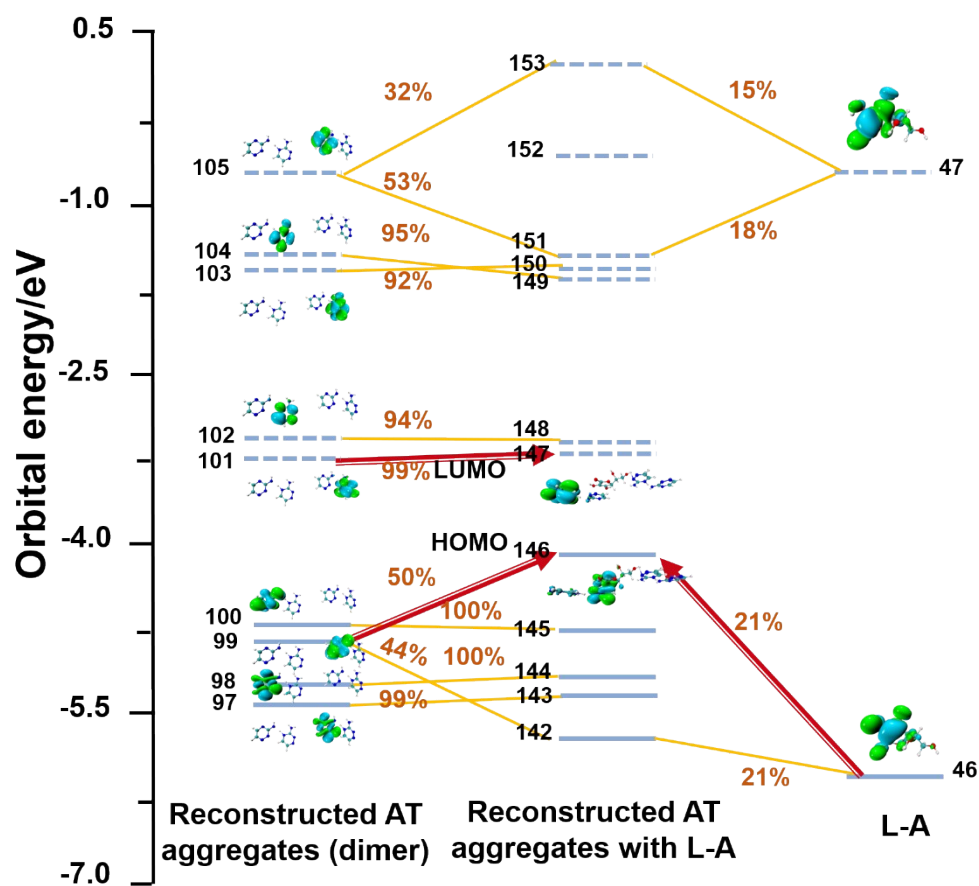
Fig. S32. Orbital interaction diagram of reconstructed AT aggregates (dimer) and L-A.
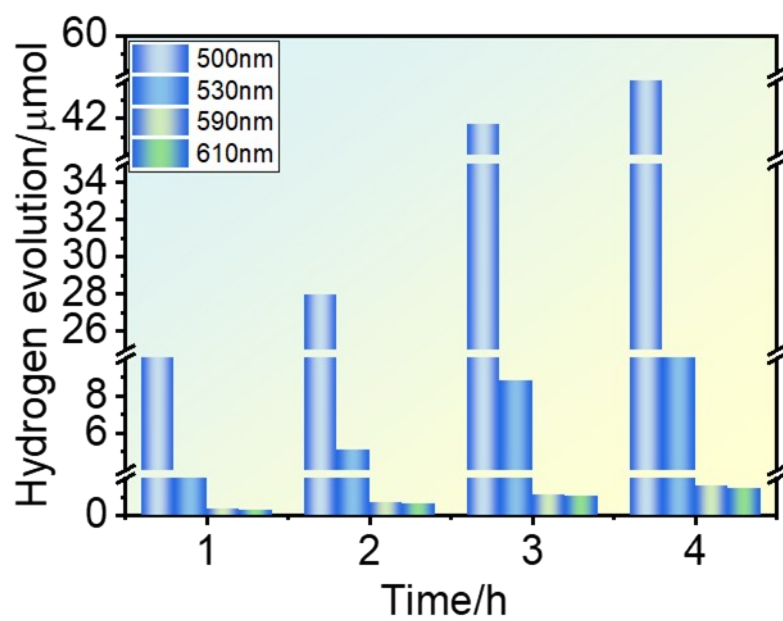
Fig. S33. Hydrogen production performance of reconstructed AT aggregates with L-A under visible and red-light irradiation (500, 530, 590, and 610 nm).
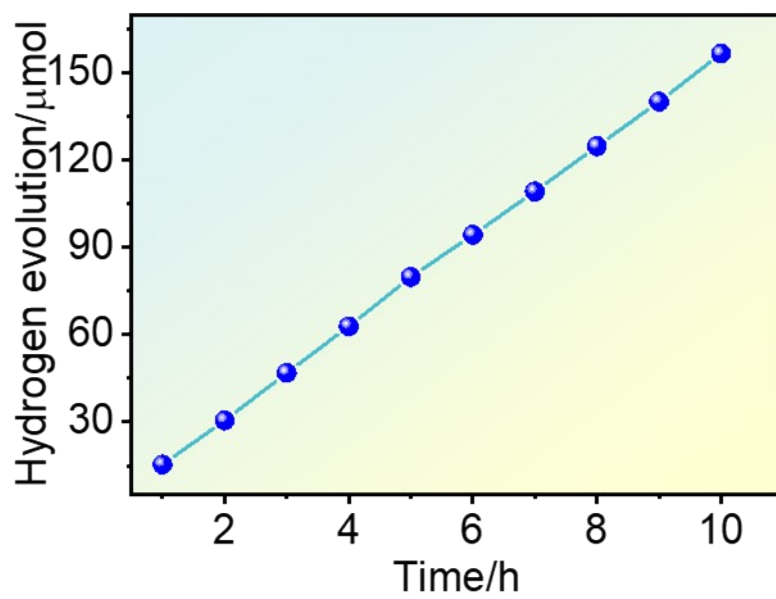
Fig. S34. Hydrogen production performance of reconstructed AT aggregates with L-A under 500 nm irradiation.
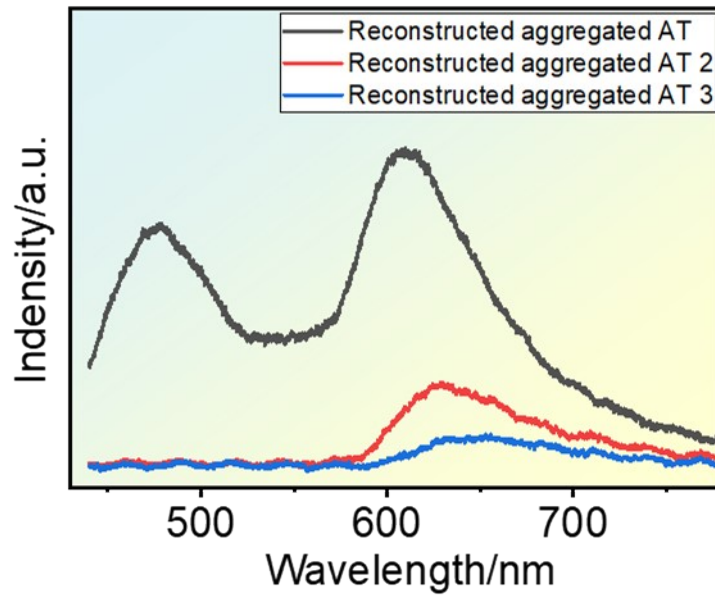
Fig. S35. PL spectra of reconstructed AT aggregates with different aggregation degrees.
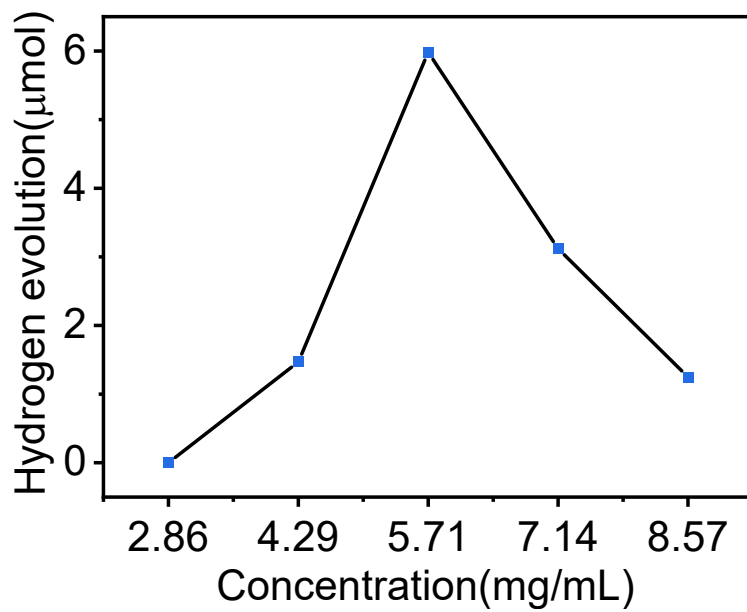
Fig. S36. Photocatalytic performances of reconstructed AT aggregates with different concentrations (reaction time: 4h; center wavelength: 850 nm; light intensity: 156 mW/cm2).

Table S1. Fitting parameters of time-resolved PL lifetime of AT aggregates and

reconstructed AT aggregates

samples	τ_1/ns	τ_2/ns	τ_3 ns	τ_{ave}/ns
AT aggregates	0.50(28.8%)	3.12(45.8%)	8.27(25.4%)	3.67 ns
Reconstructed AT aggregates	0.52(12.8%)	2.17(28.7%)	6.50(58.5%)	4.50 ns

Note: $\tau_{ave}=A_1*\tau_1^2+A_2*\tau_2^2+ A_3*\tau_3^2/ A_1*\tau_1+A_2*\tau_2+ A_3*\tau_3$

Table S2. Fitting parameters of time-resolved PL lifetime of reconstructed AT

aggregates, reconstructed AT aggregates 2 and 3

samples	τ_1/ns	τ_2/ns	$\tau_3$ns	τ_{ave}/ns
Reconstructed AT aggregates	0.56(14.9%)	2.48(31.8%)	6.87(53.3%)	4.53 ns
Reconstructed AT aggregates 2	0.57(5.2%)	3.20(56.9%)	9.54(37.9%)	5.46 ns
Reconstructed AT aggregates 3	0.84(18.3%)	4.44(62.2%)	17.01(19.6%)	6.26 ns

Note: $\tau_{ave} = A_1 * \tau_1^2 + A_2 * \tau_2^2 + A_3 * \tau_3^2 / A_1 * \tau_1 + A_2 * \tau_2 + A_3 * \tau_3$

Table S3. Comparison of hydrogen production activities with state-of-the-art photocatalysts under NIR light.

Photocatalysts	Electron donors	QYs/%	Refs.
PM6:2FBP-4F	Ascorbic acid	13.9(808 nm)	[11]
$W_{18}O_{49}$/g-C_3N_4	Triethanolamine	0.016(800 nm)	[12]
Au nanorods/$La_2Ti_2O_7$	Methanol	0.85(800 nm)	[13]
BP/TMC	Methanol	1.2(780 nm)	[14]
BP/g-C_3N_4	Methanol	1.1(780 nm)	[15]
BP/Pt/RGO	Ethylene Diamine Tetraacetic Acid	1.5(780 nm)	[16]
CdS/Cu_7S_4	Na_2S-Na_2SO_3	0.85(800 nm)	[17]
Amorphous Co_2B	Triethanolamine	1.15(800 nm)	[18]
		1.8(1000 nm)	
		3.8(1100 nm)	
Pt/CdS/NYF	----	0.008(800 nm)	[19]
TiO_2/r-GQDs	----	0.26(850 nm)	[20]
PA-Ni@PCN	Methanol	2.8(940 nm)	[21]
Reconstructed AT aggregates	Formic acid	1.23(850 nm)	This work

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