

## Supplementary Information for

# Restriction of Crossing Conical Intersections: The Intrinsic Mechanism of Aggregation-induced Emission

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### 1. UV-Vis absorption and fluorescence spectra

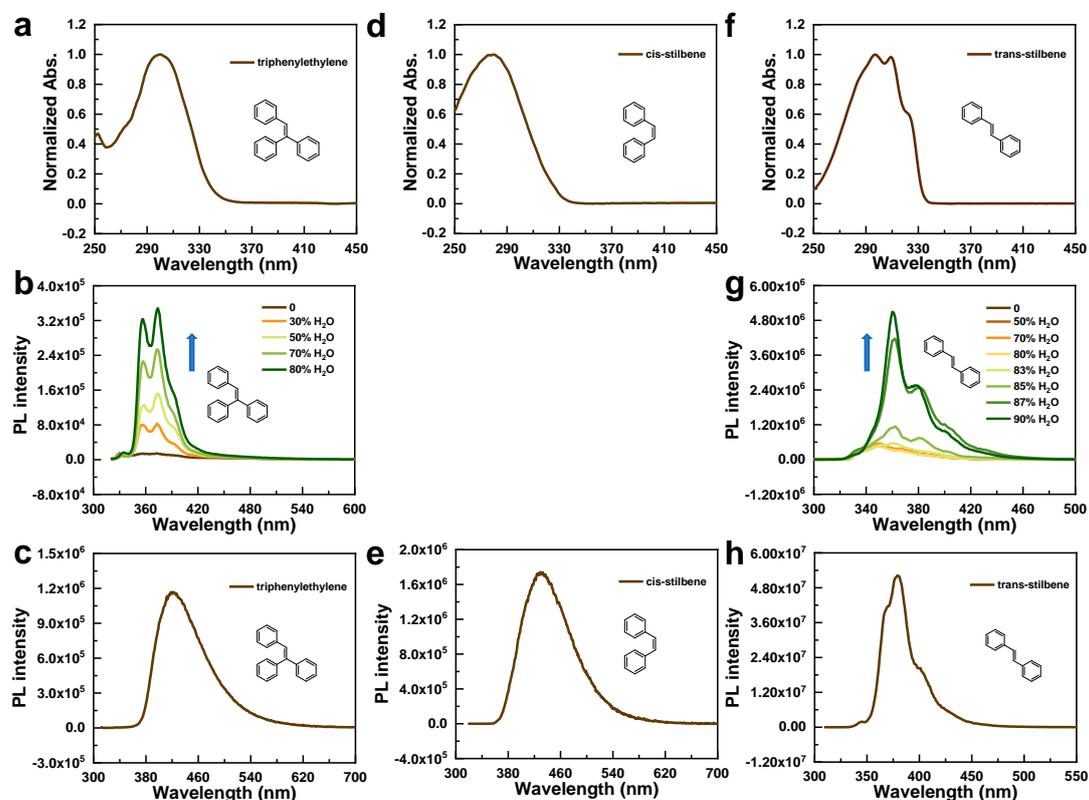
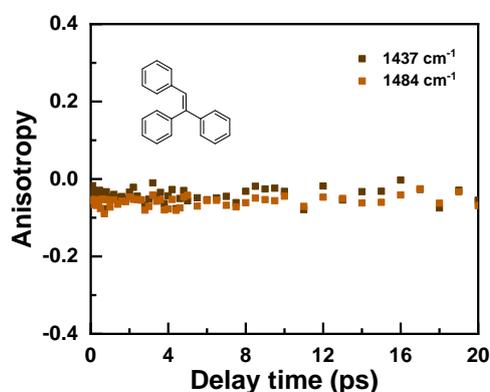


Fig. S1. UV-Vis absorption in dilute THF solution (a, d and f) and fluorescence

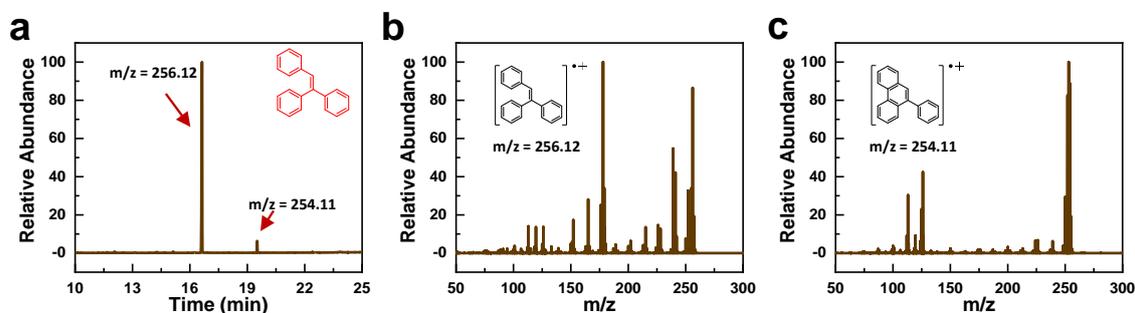
spectra in water/THF solution (b and g) and in the solid state (c, e and h) of triphenylethylene, cis-stilbene and trans-stilbene. The absorbance of the three molecules is relatively strong at 300 nm, so 300 nm is selected as the excitation wavelength for fluorescence and ultrafast experiments. In water/THF solutions, with the increase of water proportion, the fluorescence intensity of triphenylethylene and trans-stilbene in solution grows significantly, while that of cis-stilbene is too weak to detect. The fluorescence spectrum of cis-stilbene in solid is obtained at 77 K because it is liquid at room temperature.

## 2. Anisotropy of triphenylethylene in solid state



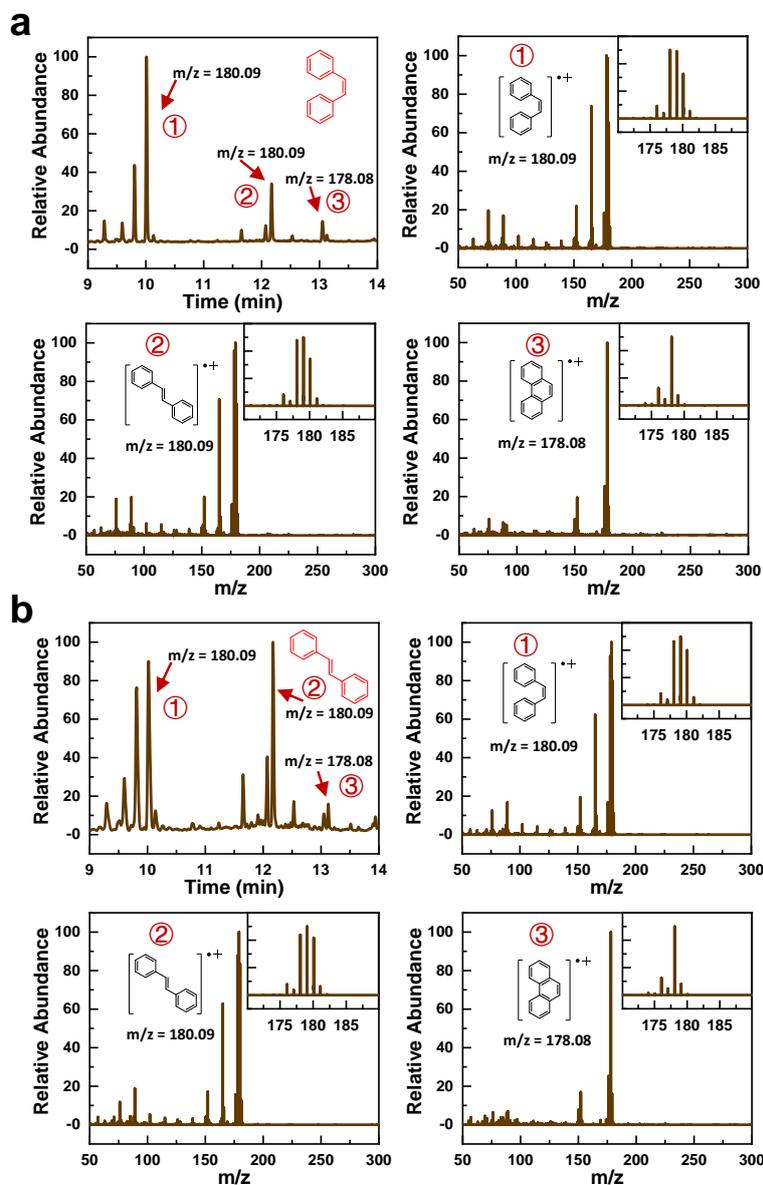
**Fig. S2.** Anisotropy of the excited absorption peaks of triphenylethylene in solid state excited with 300 nm. The anisotropy of the main peaks,  $1437\text{ cm}^{-1}$  and  $1484\text{ cm}^{-1}$ , remain constant within dozens of ps, indicating that the energy/charge transfer between molecules in the solid state is extremely weak.

## 3. GC-MS characterizations



**Fig. S3.** GC-MS characterizations of triphenylethylene after UV irradiation in THF (100 mM). (a) The elution curves and (b, c) the mass spectra of each substance eluted from the chromatographic column. A small peak assigned as the oxidation

product of the intermediate phenyl-DHP emerges, indicating the photocyclization of triphenylethylene.



**Fig. S4. GC-MS characterizations of cis-stilbene and trans-stilbene after UV irradiation in THF (100 mM).** The main elution substances of cis-stilbene and trans-stilbene are similar but the peak intensities are different. In the elution curve of the cis-stilbene solution, the peak of cis-stilbene is stronger than that of trans-stilbene, while in the solution of trans-stilbene, those two peaks are comparable, and the peak intensity of phenanthrene is relatively small in both solutions. It comes from the different stabilities and photoreaction processes of cis-stilbene and trans-stilbene in solution, that is, cis-stilbene is more stable and can be directly photocyclized and isomerized

simultaneously, while trans-stilbene first undergoes isomerization to produce cis-stilbene which is photocyclized afterwards.

#### 4. Molecular geometries of triphenylethylene and stilbene

We attach the molecular geometries of the paths in Figs. 3-4 and Figs. 7-8 of the main text as the multi-frame xyz files. The details of these xyz files are shown below. Note that we label frames starting from 0.

**Fig3(a)\_path.xyz:** The molecular geometries of the path in panel (a) of Fig. 3. The 0th, 50th and 100th represent the geometries of triphenylethylene, twist-CI and triphenylethylene (another orientation), respectively. The first 51 frames represent the path that parameterized by  $n=0, 0.02, \dots, 1$  (left side axis), respectively. The last 51 frames represent the path that is parameterized by  $m=1, 0.98, \dots, 0$  (right side axis), respectively.

**Fig3(b)\_path.xyz:** The molecular geometries of the path in panel (b) of Fig. 3. The 0-th, 50-th and 100-th represent the geometries of triphenylethylene, cyclic-CI and phenyl-DHP, respectively. The first 51 frames represent the path that parameterized by  $n=0, 0.02, \dots, 1$  (left side axis), respectively. The last 51 frames represent the path that parameterized by  $m=1, 0.98, \dots, 0$  (right side axis), respectively.

**Fig4(a)\_path.xyz:** Same as Fig3(a)\_path.xyz, but for the path in panel (a) of Fig. 4.

**Fig4(b)\_path.xyz:** Same as Fig3(b)\_path.xyz, but for the path in panel (b) of Fig. 4.

**Fig7(a)\_path.xyz:** The molecular geometries of the path in panel (a) of Fig. 7. The 0-th, 50-th and 100-th represent the geometries of trans-stilbene, twist-CI and cis-stilbene, respectively. The first 51 frames represent the path that parameterized by  $n=0, 0.02, \dots, 1$  (left side axis), respectively. The last 51 frames represent the path that

parameterized by  $m = 1, 0.98, \dots, 0$  (right side axis), respectively.

**Fig7(b)\_path.xyz:** The molecular geometries of the path in panel (b) of Fig. 7. The 0th, 50th and 100th represent the geometries of cis-stilbene, cyclic-CI and DHP, respectively. The first 51 frames represent the path that parameterized by  $n = 0, 0.02, \dots, 1$  (left side axis), respectively. The last 51 frames represent the path that parameterized by  $m = 1, 0.98, \dots, 0$  (right side axis), respectively.

**Fig8(a)\_path.xyz:** Same as Fig7(a)\_path.xyz, but for the path in panel (a) of Fig. 8.

**Fig8(b)\_path.xyz:** Same as Fig7(b)\_path.xyz, but for the path in panel (b) of Fig. 8.