# Dynamics of aggregated states resolved by gated fluorescence in films of room temperature phosphorescent emitters

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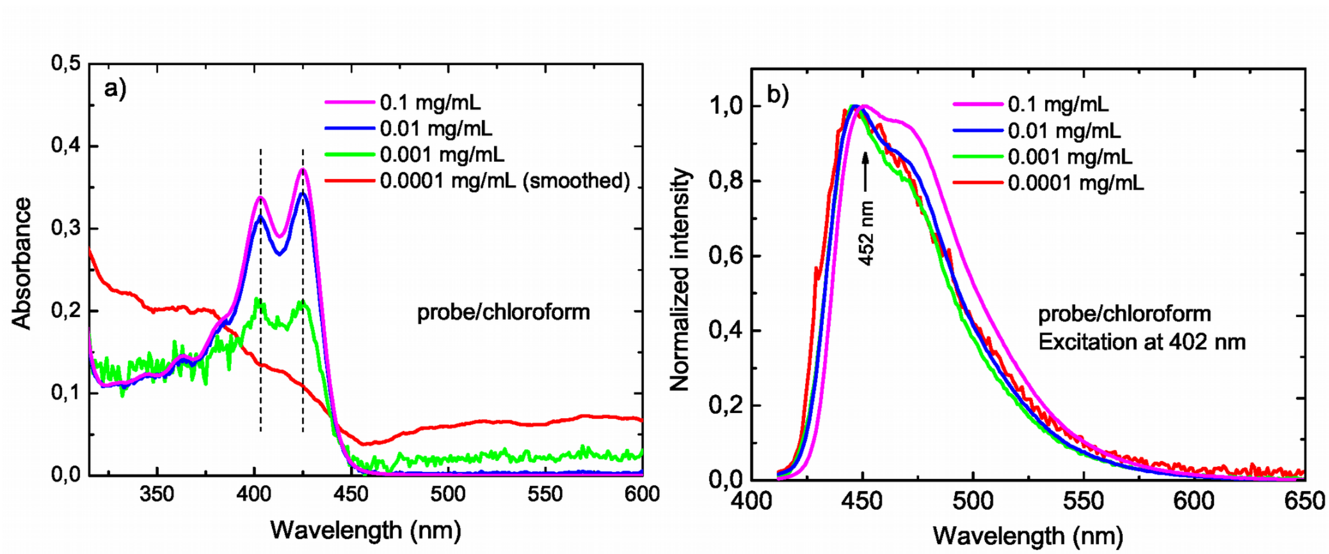


Figure S1: (a) Absorption and (b) Emission spectra at relatively low concentration of probe solutions in chloroform.

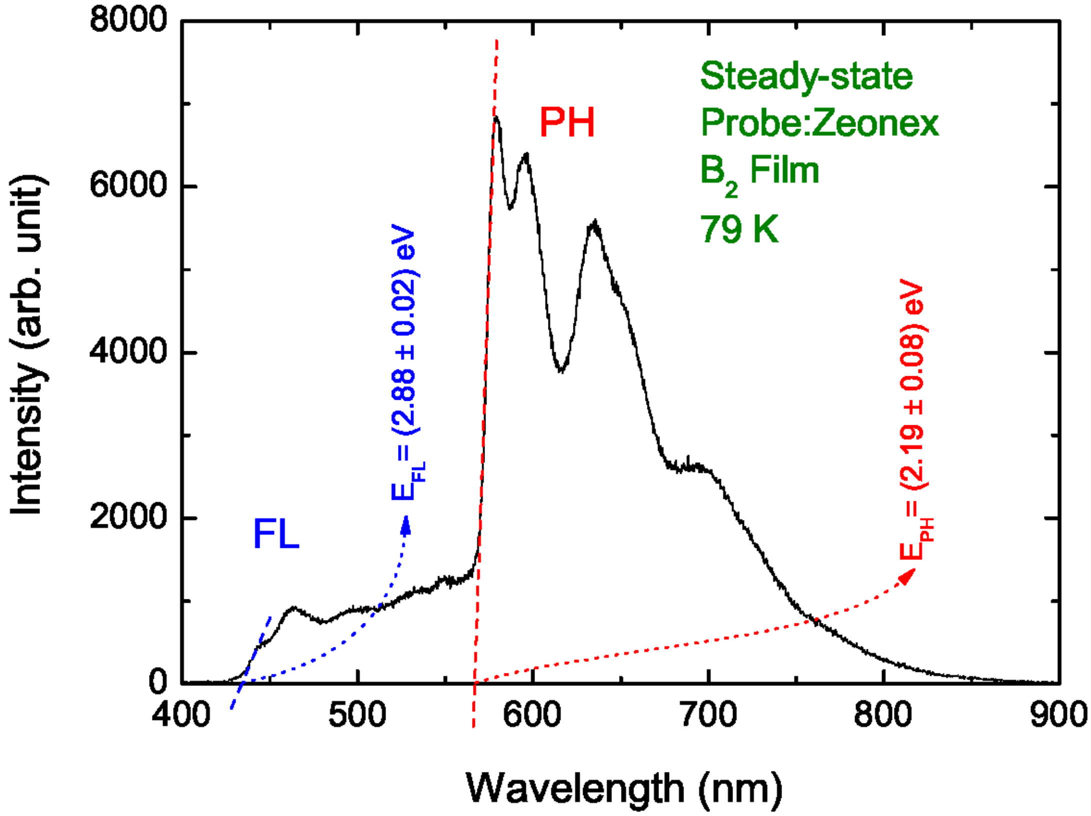


Figure S2: Steady-state emission spectrum of film B2 at 79 K. The FL and PH energies,indicated by arrows, were estimated from the respective onset lines.

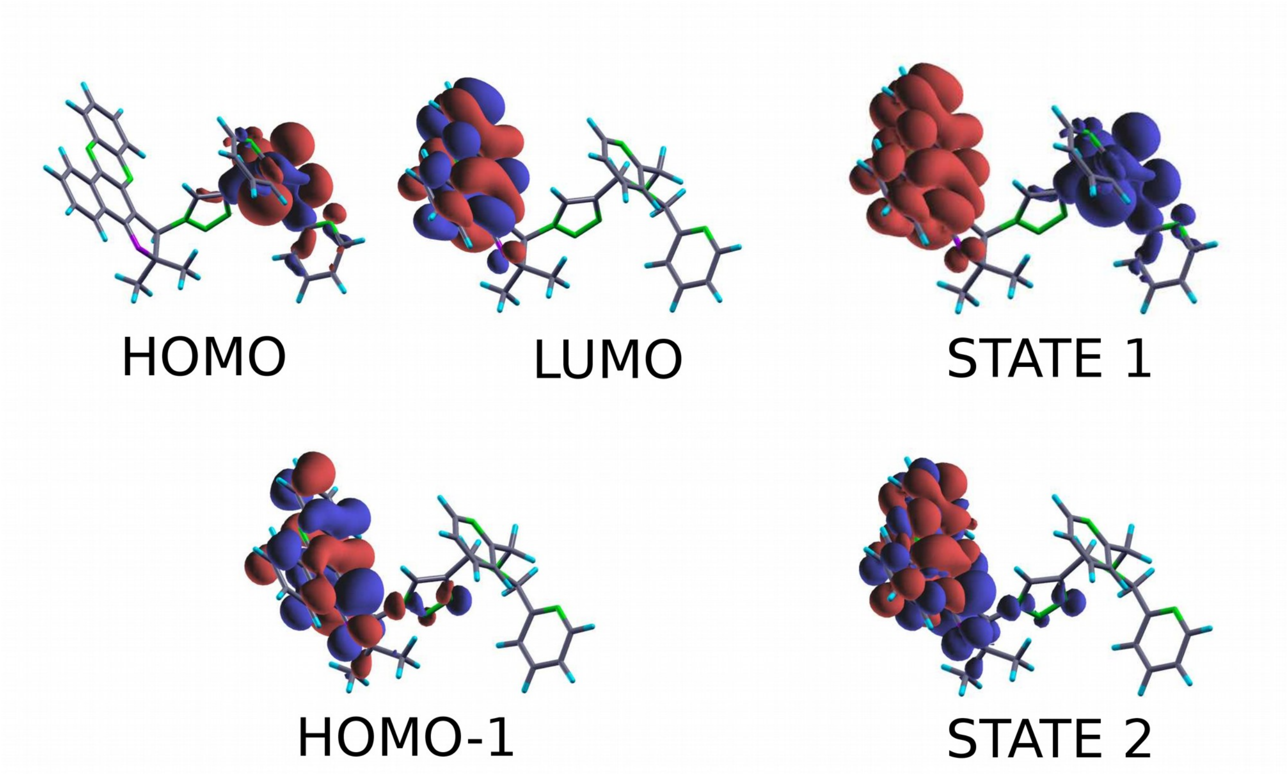


Figure S3: Molecular orbital plots for the HOMO-1, HOMO and LUMO of the monomer and the TDDFT difference densities for state 1 and 2 calculated with the B3LYP functional. In TDDFT difference densities, blue indicates a loss of electron density upon excitation and red indicates a gain of electron density. The TDDFT difference density for state 1 indicates an excitation from a molecular orbital localized on the N,N-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine (HOMO) to a molecular orbital on the planar phenazine compound (LUMO), and exhibits very small oscillator strength (Table 1). The state 2 shows the TDDFT difference density for the transition from HOMO-1 to LUMO, which corresponds to an excitation localized on the phenazine compound plane and contribute to an intense peak on the UVvis spectrum. The molecular orbitals obtained with PBE0 are very similar, so the TDDFT difference densities must not differ.

Table S1: Energy λ (in nm), oscillator strength $f_{osc}$, and orbitals that have relevant contributions to the electronic transitions of the monomer calculated with TDDFT/B3LYP and TDDFT/PBE0 (PBE0 calculation with fixed geometry from B3LYP). In main transitions, the orbitals 151 and 152 are the HOMO and LUMO, respectively.

| | B3LYP | | | PBE0 | | |
|---|---|---|---|---|---|---|
| state | λ (nm) | $f_{osc}$ | Main transitions (≥ 10%) | λ (nm) | $f_{osc}$ | Main transitions (≥ 10%) |
| 1 | 455.6 | 0.0000 | 151 → 152 (100%) | 420.4 | 0.0000 | 151 → 152 (100%) |
| 2 | 388.1 | 0.1244 | 147 → 152 (12%)<br>150 → 152 (74%) | 378.1 | 0.0353 | 145 → 152 (25%)<br>147 → 152 (43%)<br>150 → 152 (18%) |
| 3 | 384.9 | 0.0259 | 147 → 152 (65%)<br>150 → 152 (14%) | 374.9 | 0.1351 | 147 → 152 (11%)<br>150 → 152 (70%) |
| 4 | 340.6 | 0.0406 | 149 → 152 (71%)<br>150 → 153 (22%) | 331.0 | 0.0450 | 149 → 152 (72%)<br>150 → 153 (21%) |

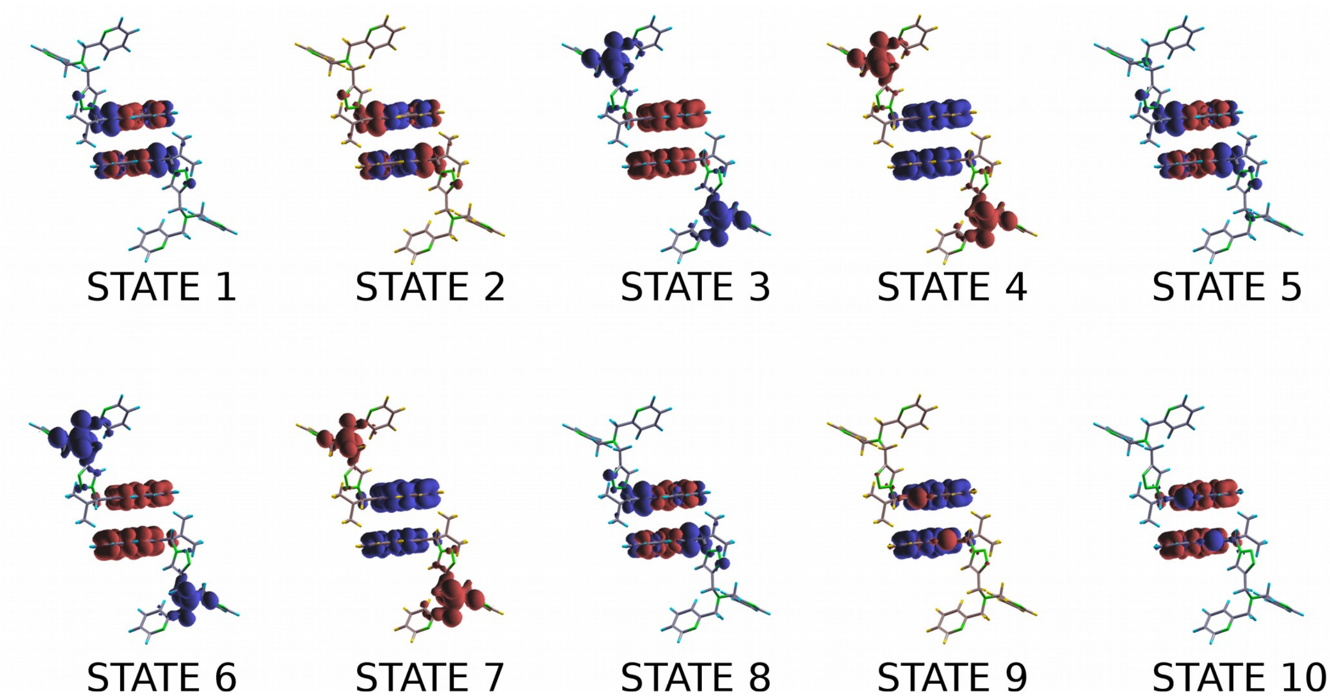


Figure S4: TDDFT difference densities for state 1 to 10 of the dimer calculated with the B3LYP functional. In TDDFT difference densities, blue indicates a loss of electron density upon excitation and red indicates a gain of electron density. The molecular orbitals obtained with PBE0 are very similar, so the TDDFT difference densities must not differ.

Table *S2:* Energy λ (in nm), oscillator strength $f_{osc}$, and orbitals that have relevant contributions to the electronic transitions of the dimer calculated with TDDFT/B3LYP and TDDFT/PBE0 (PBE0 calculation with fixed geometry from B3LYP). For the dimer, several molecular orbitals are degenerated, for example, 302 and 303 orbitals are the HOMO while the 304 and 305 are the LUMO. The 300 and 301 orbitals have contribution on several main transitions shown in this Table, and both are the degenerate HOMO-1.

| | B3LYP | | | PBE0 | | |
|---|---|---|---|---|---|---|
| state | λ (nm) | $f_{osc}$ | Main transitions (≥ 10%) | λ (nm) | $f_{osc}$ | Main transitions (≥ 10%) |
| 1 | 417.5 | 0.0000 | 300→ 304 (53%)<br>301 → 305 (45%) | 393.2 | 0.0009 | 300→ 304 (54%)<br>301→ 305 (42%) |
| 2 | 417.4 | 0.0005 | 300 → 305 (44%)<br>301 → 304 (54%) | 393.2 | 0.0008 | 300 → 305 (36%)<br>301 → 304 (60%) |
| 3 | 406.2 | 0.0003 | 302 → 304 (10%)<br>303 → 305 (11%)<br>302 → 305 (36%)<br>303 → 304 (43%) | 385.7 | 0.0061 | 300 → 305 (55%)<br>301 → 304 (31%) |
| 4 | 406.1 | 0.0008 | 302 → 304 (43%)<br>303 → 305 (36%)<br>302 → 305 (11%)<br>303 → 304 (10%) | 378.1 | 0.1335 | 300 → 304 (19%)<br>301 → 305 (23%)<br>302 → 304 (14%)<br>303 → 305 (14%) |
| 5 | 398.3 | 0.0314 | 300 → 305 (50%)<br>301 → 304 (40%) | 377.0 | 0.0027 | 288 → 305 (21%)<br>289 → 304 (19%)<br>302 → 305 (20%)<br>303 → 304 (23%) |
| 6 | 392.7 | 0.0000 | 302 → 304 (30%)<br>303 → 304 (16%)<br>303 → 305 (47%) | 377.0 | 0.0006 | 288 → 304 (17%)<br>289 → 305 (14%)<br>302 → 304 (28%)<br>303 → 305 (26%) |
| 7 | 392.7 | 0.0000 | 302 → 304 (16%)<br>302 → 305 (47%)<br>303 → 304 (30%) | 376.6 | 0.0029 | 288 → 305 (17%)<br>389 → 304 (15%)<br>302 → 305 (24%)<br>303 → 304 (26%) |
| 8 | 390.1 | 0.2251 | 300 → 304 (39%)<br>301 → 305 (46%) | 375.5 | 0.0832 | 288 → 304 (14%)<br>289 → 305 (11%)<br>300 → 304 (18%)<br>301 → 305 (25%) |
| 9 | 384.3 | 0.0072 | 290 → 305 (35%)<br>291 → 304 (33%)<br>293 → 304 (14%) | 362.6 | 0.0000 | 302 → 304 (24%)<br>302 → 305 (15%)<br>303 → 304 (22%)<br>303 → 305 (36%) |
| 10 | 384.0 | 0.0045 | 290 → 304 (36%)<br>291 → 305 (31%)<br>293 → 305 (13%) | 362.6 | 0.0000 | 302 → 304 (22%)<br>302 → 305 (36%)<br>303 → 304 (24%)<br>303 → 305 (15%) |