

Supporting Information for
Engineering Giant Excitonic Coupling
In Bioinspired, Covalently Bridged BODIPY Dyads

Sara Ansteatt,[†] Brian Uthe,[‡] Bikash Mandal,[§] Rachel S. Gelfand,[‡] Barry D. Dunietz,^{*,§}
Matthew Pelton,^{*,†,‡} and Marcin Ptaszek^{*,†}

[†]Department of Chemistry and Biochemistry
[‡]Department of Physics
University of Maryland, Baltimore County
1000 Hilltop Circle
Baltimore, MD 21250

[§]Department of Chemistry and Biochemistry
Kent State University
Kent, OH 44242

*corresponding authors

mptaszek@umbc.edu (M. Ptaszek)

mpelton@umbc.edu (M. Pelton)

bdunietz@kent.edu (B. D. Dunietz)

Contents

| | |
|---|------------|
| S1. <i>trans-cis</i> Photoisomerization of <i>trans</i>-β-2BDP-F. | S3 |
| S2. Selected geometrical parameters for dyads. | S3 |
| S3. Additional absorption and emission spectra | S4 |
| S4. Deconvolution of absorption spectra of | S6 |
| S5. Time-resolved fluorescence. | S8 |
| S6. Transient absorption spectra | S9 |
| S7. Additional computational results | S12 |
| S8. Structures of “disconnected” dyads. | S16 |

S1. *trans-cis* Photoisomerization of *trans*- β -2BDP-F

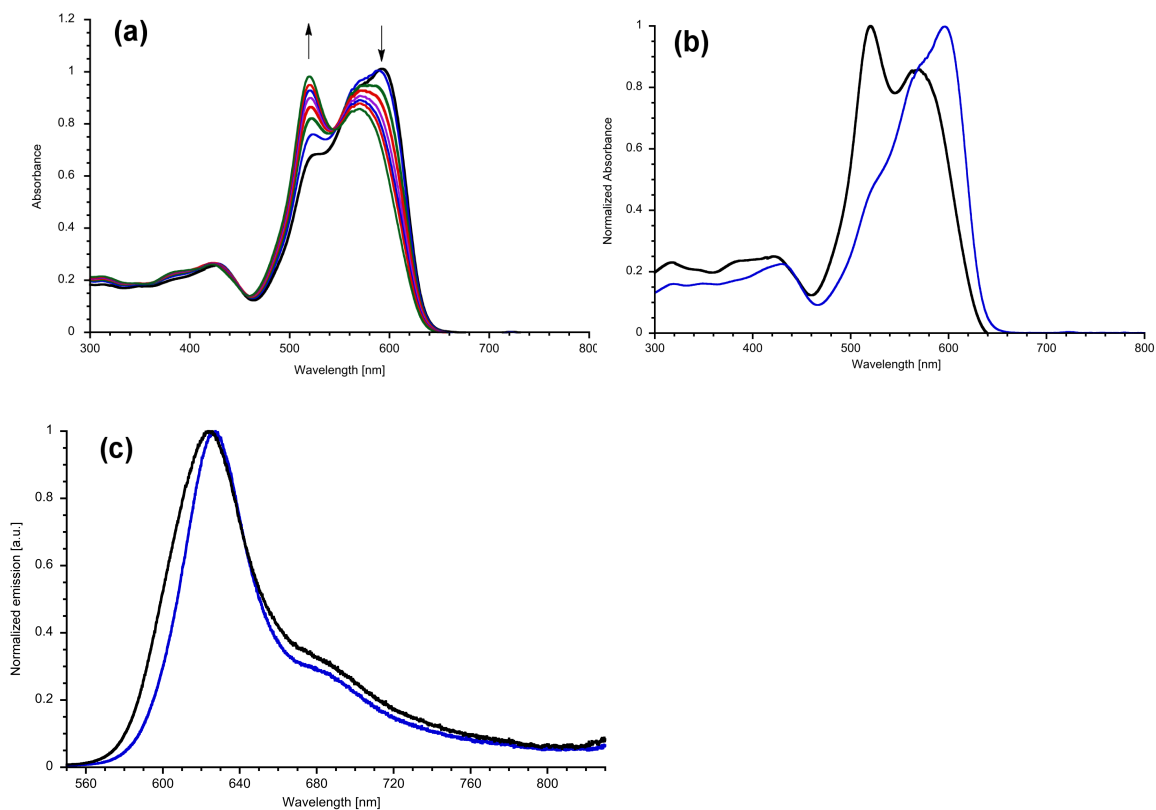


Figure S1. (a) Changes in absorption spectrum of *trans*- β -2BDP-F upon irradiation at 594 nm in toluene. Absorption spectra were taken in 30 sec. intervals. (b) Normalized absorption spectra of *trans*- β -2BDP-F (blue) and *cis*- β -2BDP-F (black) in toluene. (c) Emission spectra of *trans*- β -2BDP-F (blue) and *cis*- β -2BDP-F (black) in toluene.

S2. Selected geometrical parameters for dyads.

Table S1. Geometrical Parameters for BDP dyads.

| Dyad | α | ϕ | θ |
|------------------------------|----------|--------|----------|
| β -2BDP-M | 3.23 | 0.95 | 89.06 |
| β -2BDP-B | 14.43 | 8.60 | 79.80 |
| <i>cis</i> - β -2BDP-F | 53.55 | 31.79 | 64.15 |
| β -2BDP-X | 4.17 | 3.45 | 85.64 |

α – is an angle between transition dipole moments for BODIPY sub-units; ϕ is an angle between mean BODIPY planes; θ is an angle between transition dipole moments and a line connecting the centers of the BODIPY subunits (for $\theta < 54.7^\circ$ J aggregate, for $\theta > 54.7^\circ$ – H aggregate).

S3. Additional absorption and emission spectra

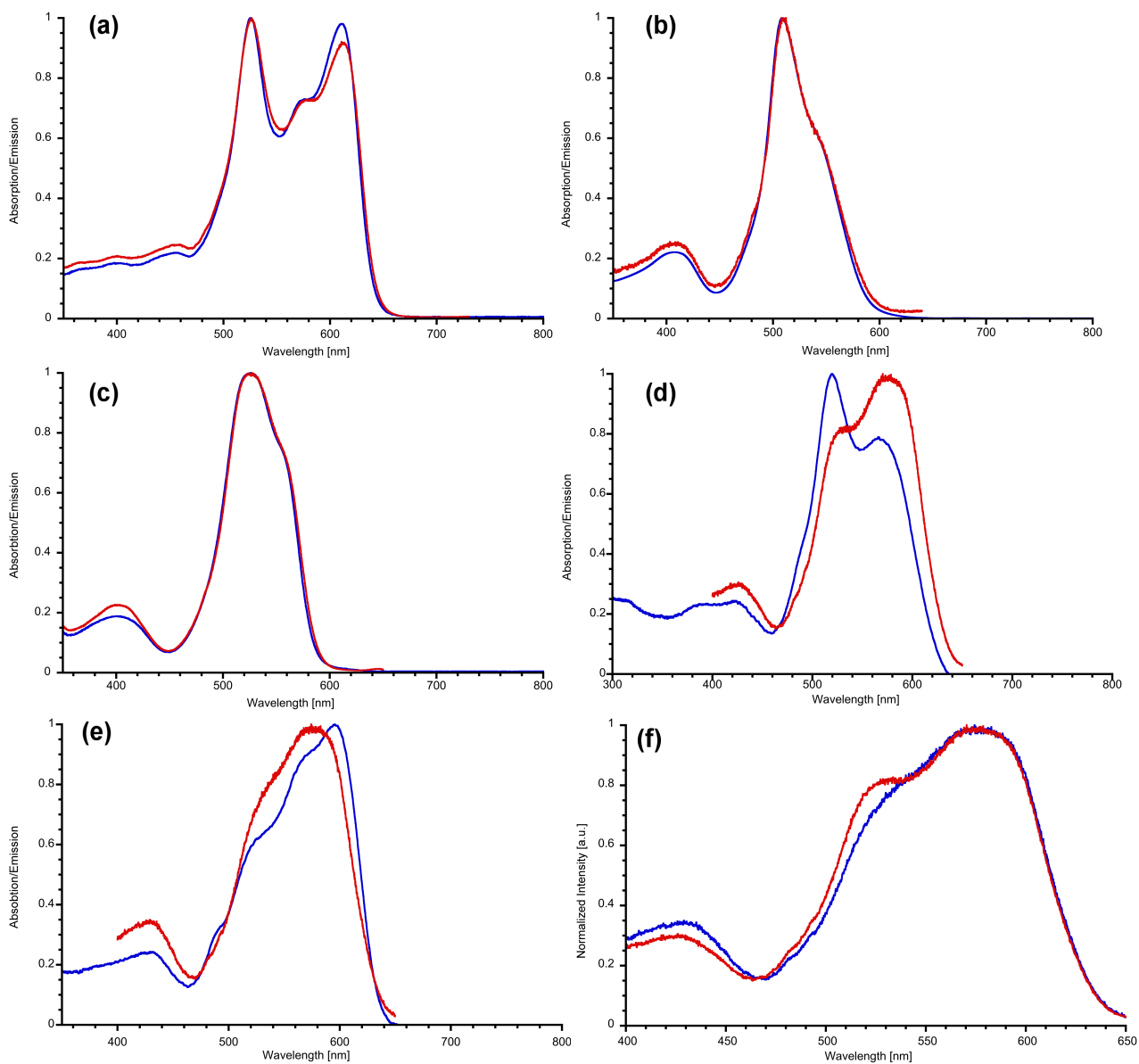


Figure S2. Absorption (blue) and excitation (red) spectra of (a) β -2BDP-M, (b) β -2BDP-X, (c) β -2BDP-B, (d) *cis*- β -2BDP-F, and (e) *trans*- β -2BDP-F. (f) Comparison of excitation spectra for *trans*- β -2BDP-F (blue) and *cis*- β -2BDP-F (red). All spectra were taken in toluene.

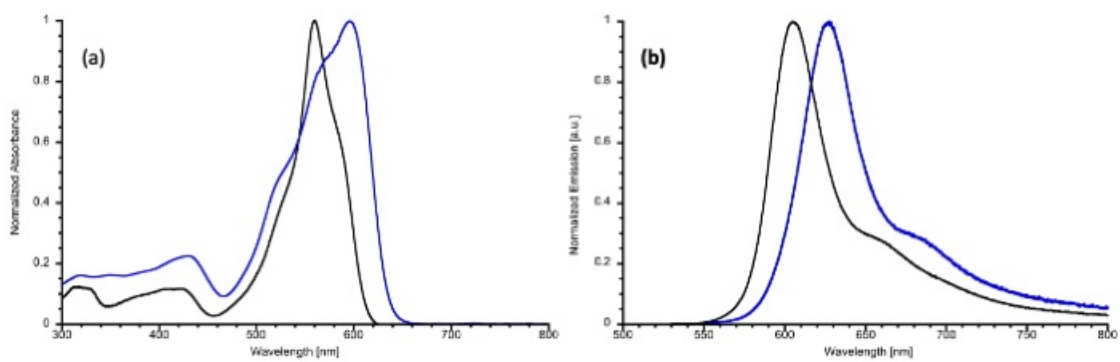


Figure S3. (a) Absorption and (b) emission spectra for β -2BDP-H (black) and *trans*- β -2BDP-F (blue) in toluene. For emission spectra, samples were excited at the maximum of corresponding $S_0 \rightarrow S_2$ absorption band.

S4. Deconvolution of absorption spectra

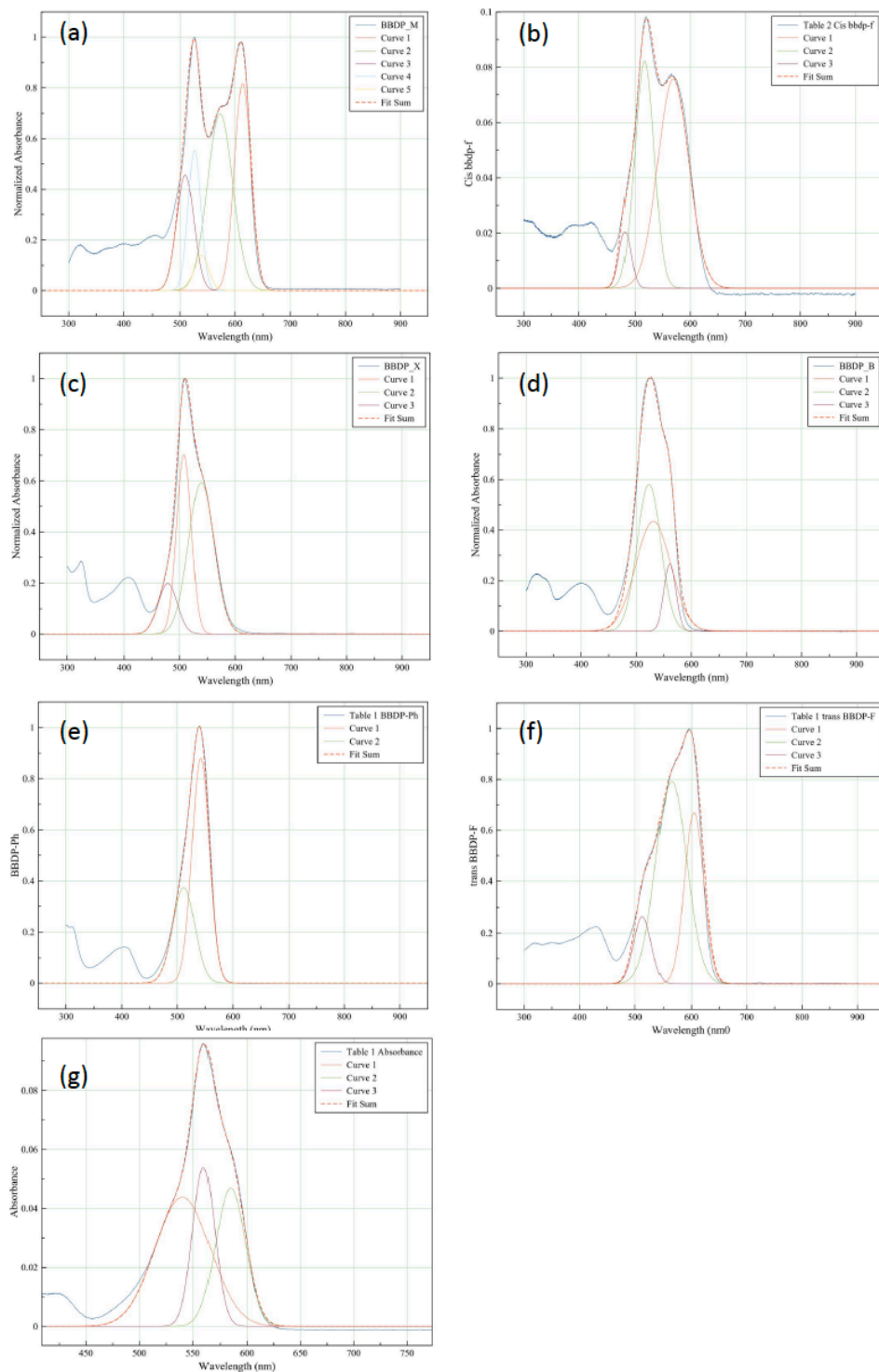


Figure S4. Fitting of absorption spectra with multiple Gaussian curves for (a) β -2BDP-M, (b) *cis*- β -2BDP-F, (c) β -2BDP-X, (d) β -2BDP-B, (e) β -BDP-Ph, (f) *trans*- β -2BDP-F and (g) β -2BDP-H in toluene.

Table S2. Absorption-band maxima obtained from deconvolution of the main absorption manifold (in toluene) into Gaussian bands. The absorption band splitting **DE** is the energy difference between the highest-energy and lowest-energy band of the visible absorption manifold.

| Compound | λ_{\max} (nm) |
|--|---|
| β-2BDP-M | 509, 526, 538, 572, 613 |
| β-2BDP-B | 523, 530, 561 |
| β-2BDP-X | 478, 507, 538 |
| cis-β-2BDP-F | 482, 517, 569 |
| trans-β-2BDP-F | 513, 564, 604 |
| β-2BDP-H | 540, 560, 585, 560 |
| β-BDP-Ph | 511, 542 |

S5. Time-resolved fluorescence

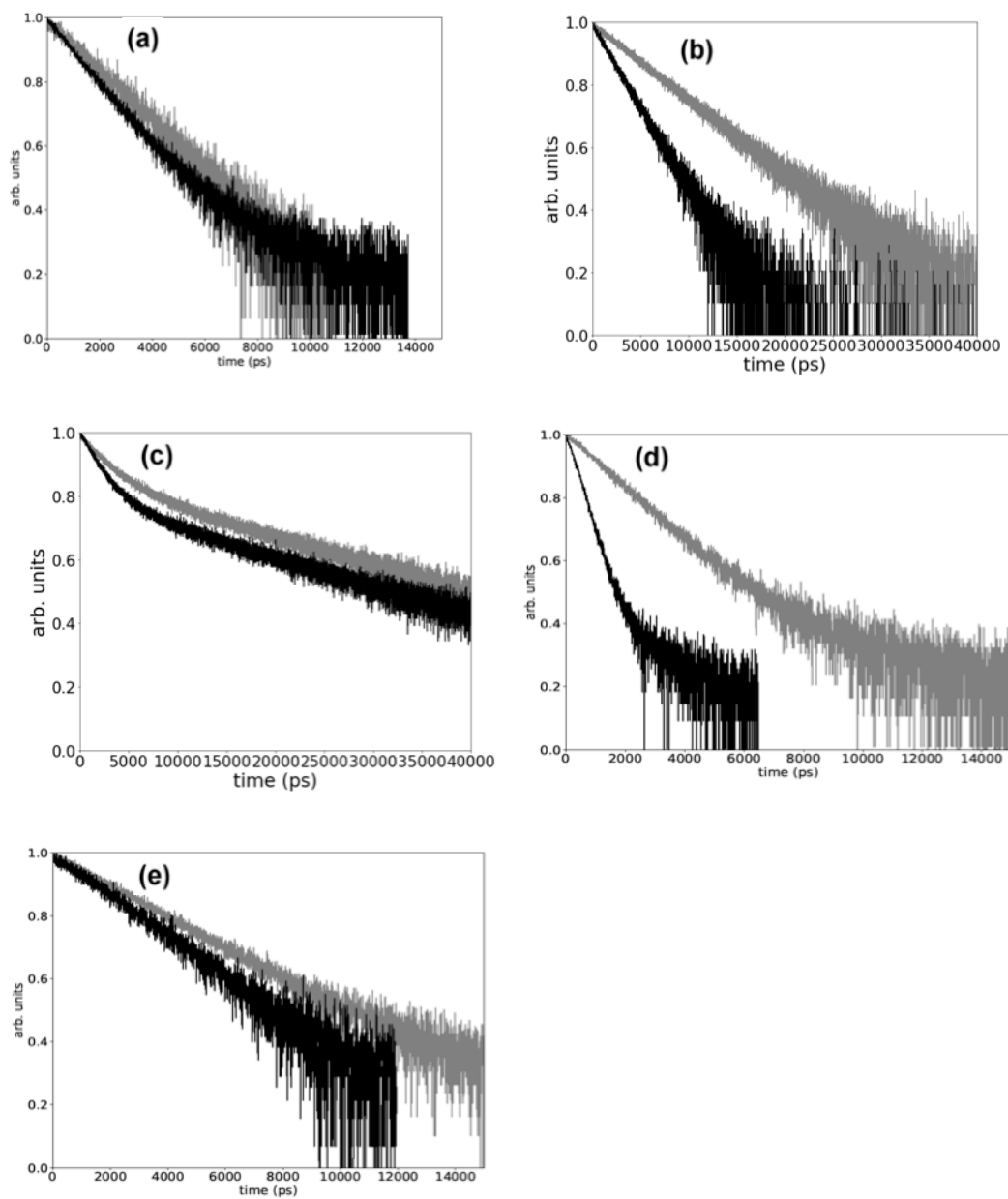


Figure S5. Time resolved fluorescence in toluene (grey) and PhCN (black) for (a) β -2BDP-M (b) β -2BDP-B, (c) β -2BDP-X, (d) β -2BDP-H, and (e) β -BDP-Ph

S6. Transient-absorption spectra

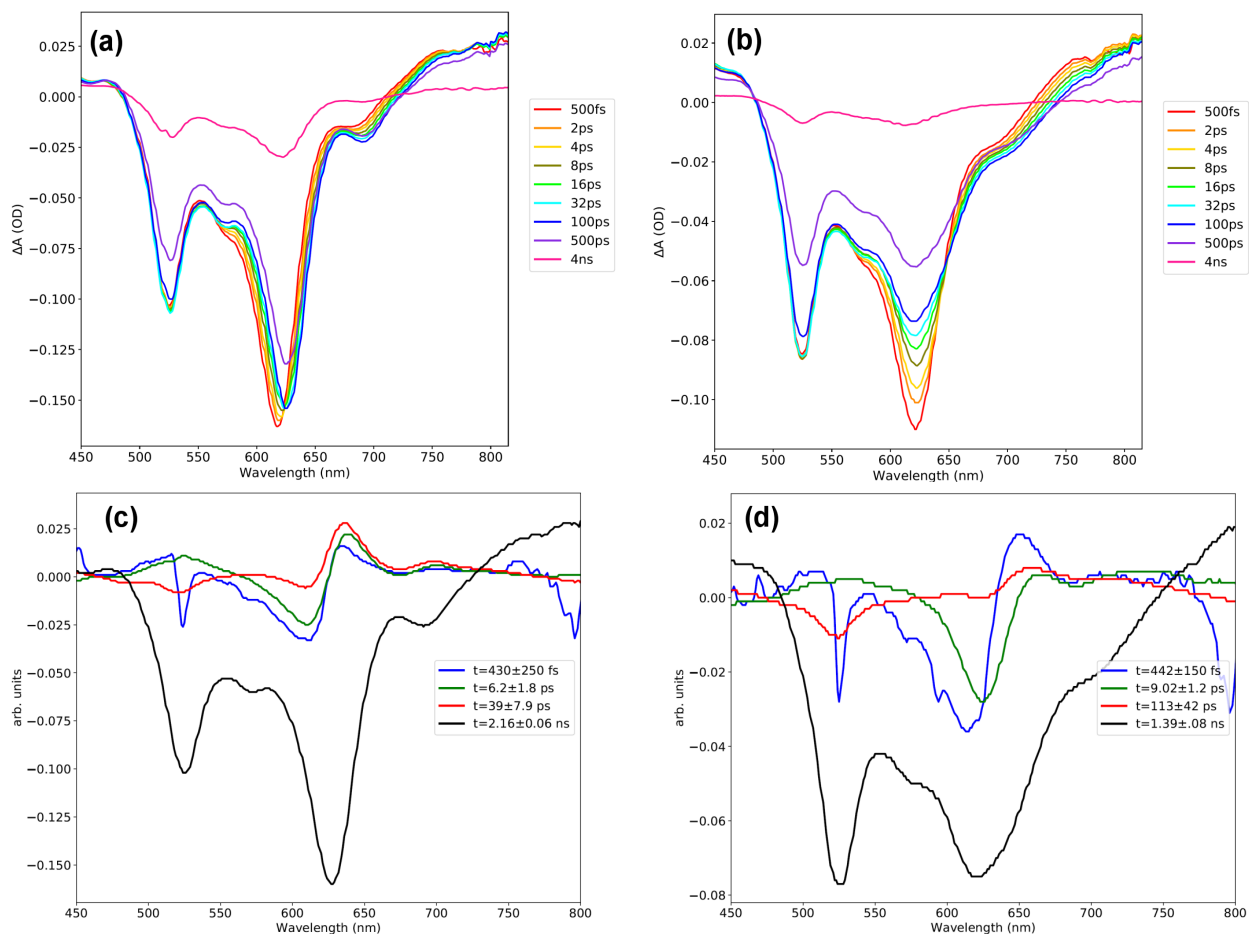


Figure S6. Transient absorption spectra of β -2BDP-M in (a) toluene and (b) PhCN for pump wavelength of 526 nm, together with DADS of kinetic components (c) in toluene and (d) in PhCN.

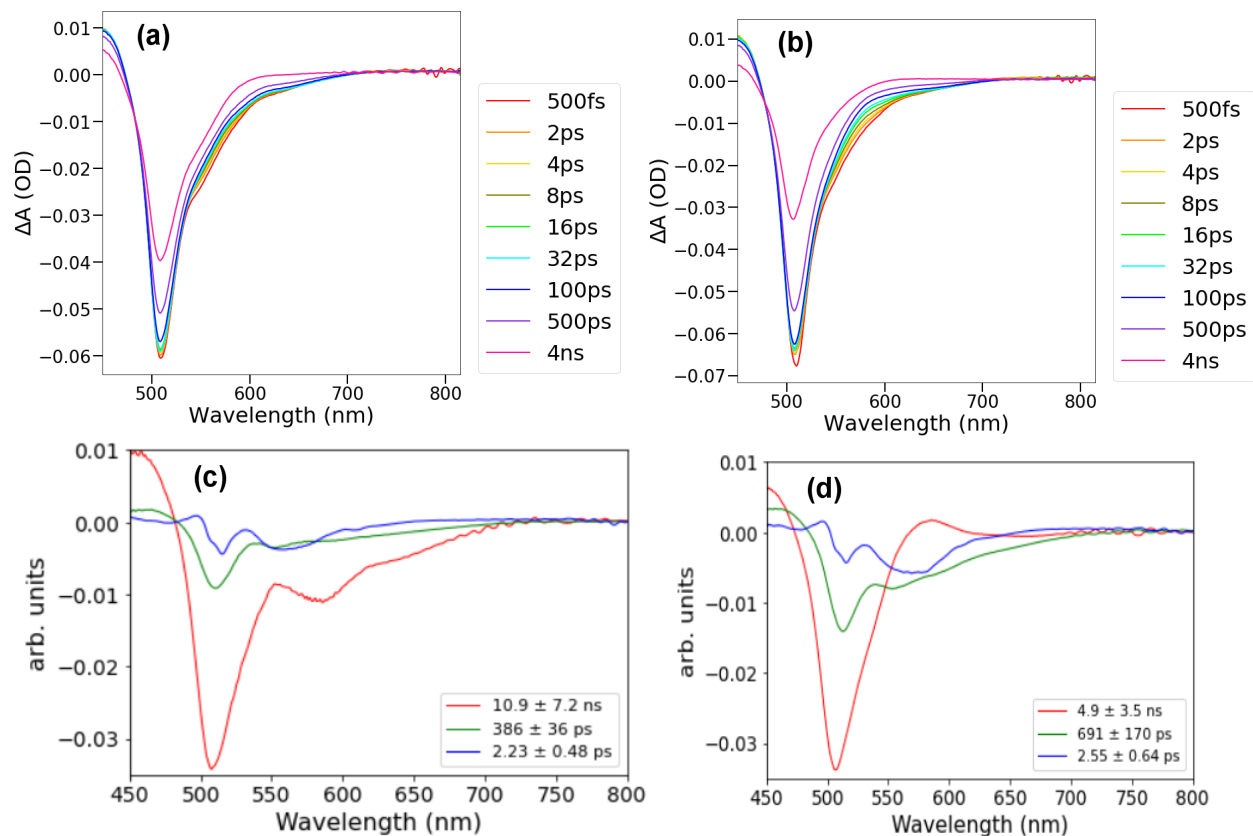


Figure S7. Transient absorption spectra of β -2BDP-X in (a) toluene and (b) PhCN for pump wavelength of 509 nm, together with DADS of kinetic components (c) in toluene and (d) in PhCN. The short-lived component (< 300 fs) was omitted as is too close to the temporal resolution of the instrument (150 fs).

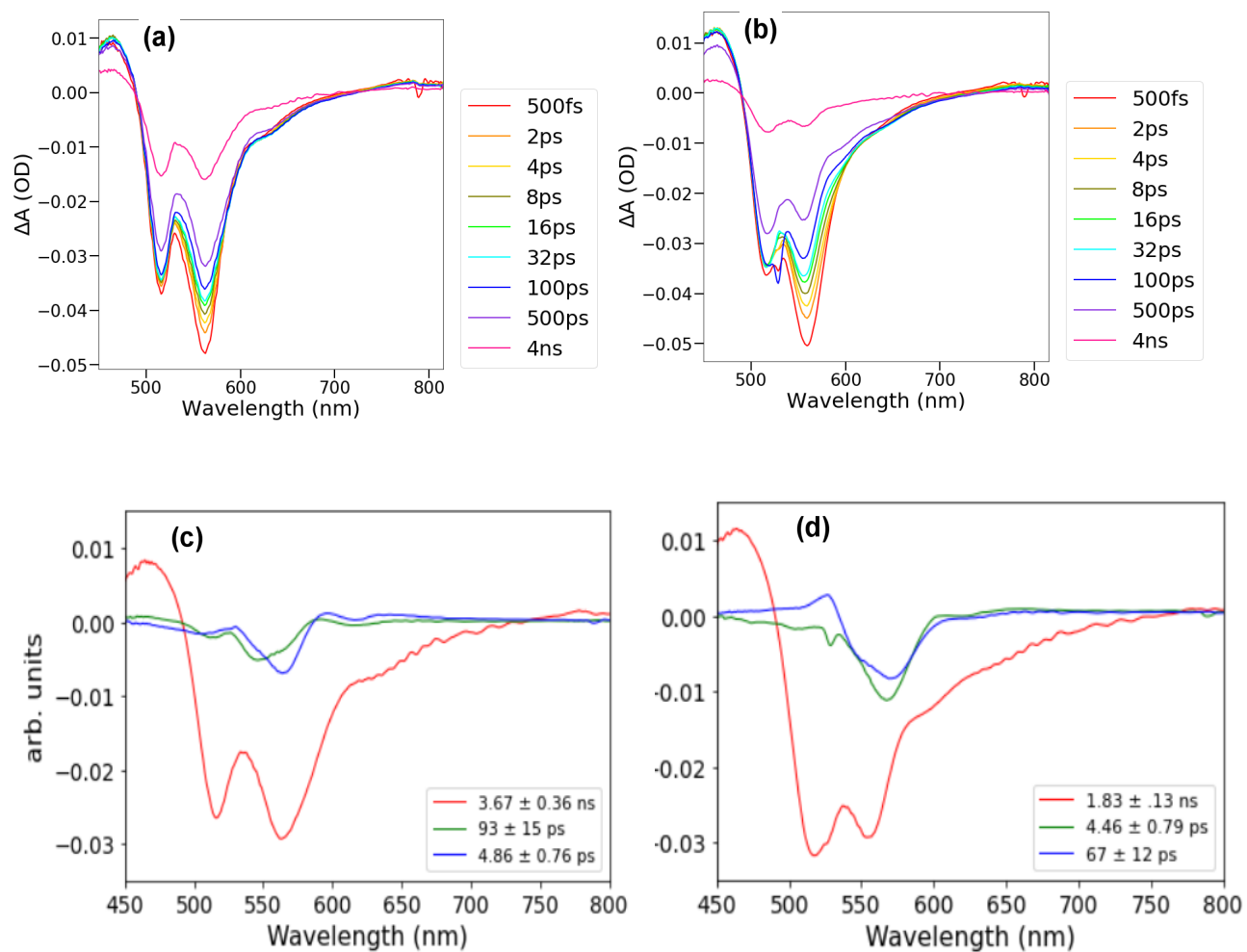


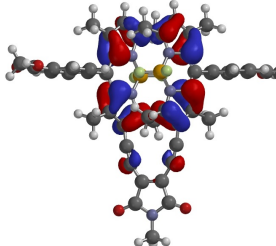
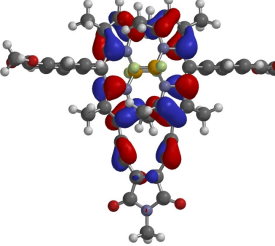
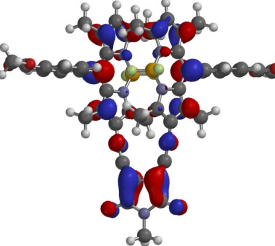
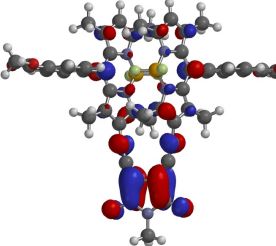
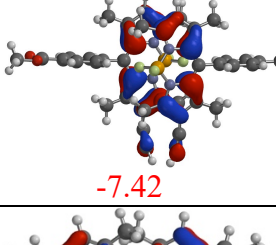
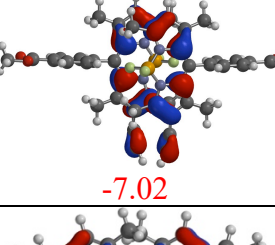
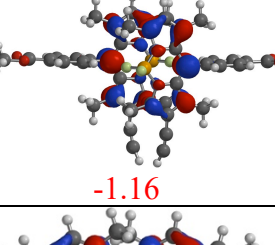
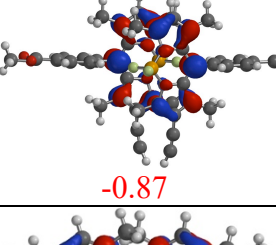
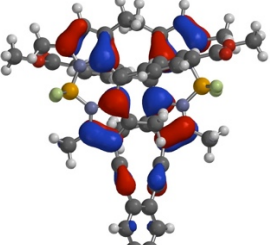
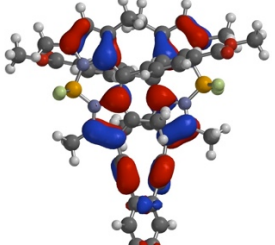
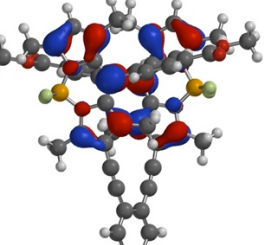
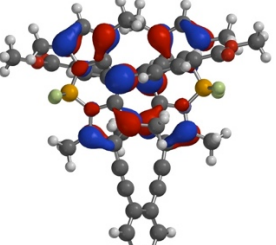
Figure S8. Transient absorption spectra of β -2BDP-B in (a) toluene and (b) PhCN for pump wavelength of 526 nm, together with DADS of kinetic components (c) in toluene and (d) in PhCN. The short-lived component (< 300 fs) was omitted as is too close to the temporal resolution of the instrument (150 fs).

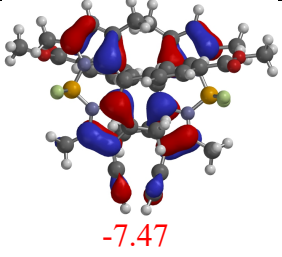
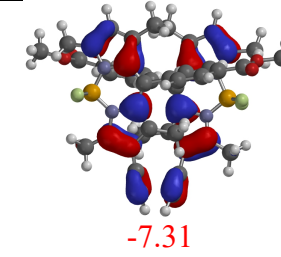
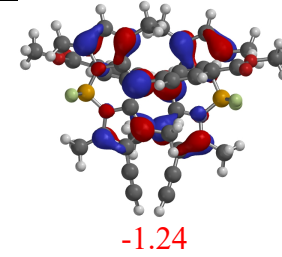
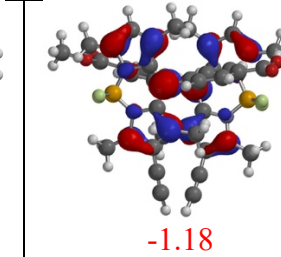
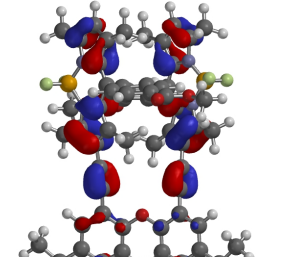
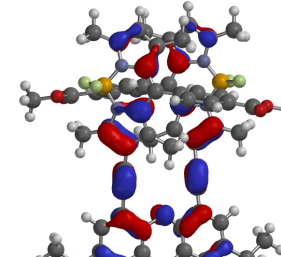
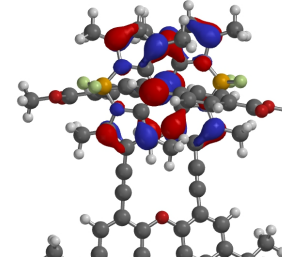
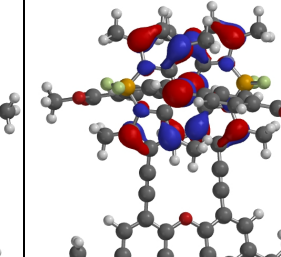
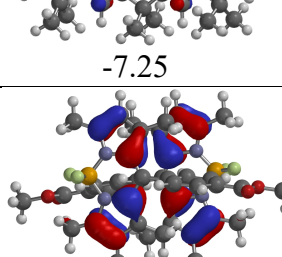
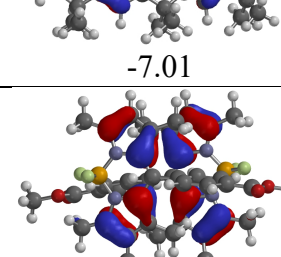
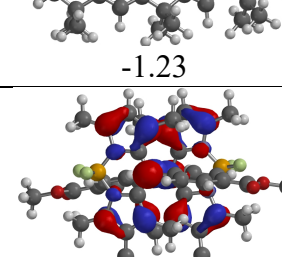
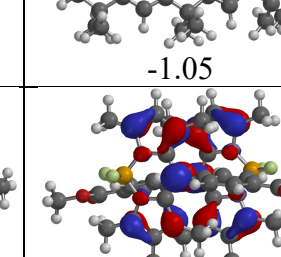
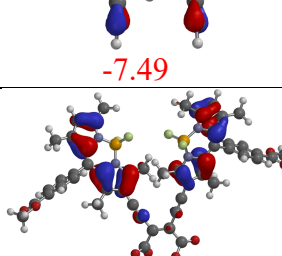
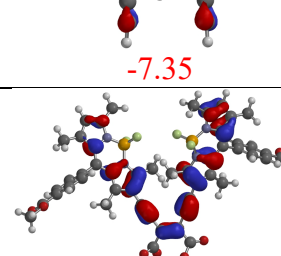
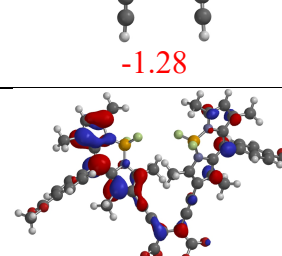
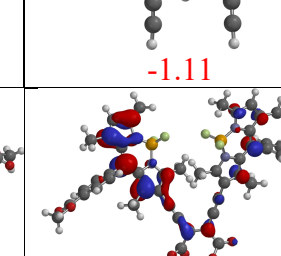
S7. Additional computational results

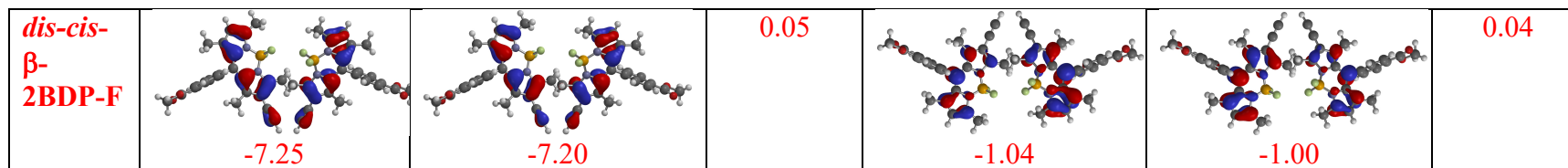
Table S3. Molecular-orbital energies using the PCM model without the polarization-consistent screening framework. Geometries are optimized in toluene using wb97xd. The calculated IP and EA of the monomer at this level of calculations are 6.88 and -1.97 eV, respectively. Note the large deviation of the HOMO energy from the ionization potential and the LUMO energy from the electron affinity.

| Dyad | HOMO-1 | HOMO | $\Delta(\text{HOMO})$ | LUMO | LUMO+1 | $\Delta(\text{LUMO})$ |
|---|--------|-------|-----------------------|-------|--------|-----------------------|
| β-2BDP-M | -7.78 | -7.34 | 0.44 | -1.63 | -1.33 | 0.30 |
| <i>dis-β</i> - 2BDP-M | -7.64 | -7.24 | 0.40 | -1.39 | -1.09 | 0.30 |
| β-2BDP-B | -7.64 | -7.43 | 0.21 | -1.47 | -1.39 | 0.08 |
| <i>dis-β</i> - 2BDP-B | -7.70 | -7.53 | 0.17 | -1.47 | -1.41 | 0.06 |
| β-2BDP-X | -7.45 | -7.21 | 0.24 | -1.44 | -1.25 | 0.19 |
| <i>dis-β</i> - 2BDP-X | -7.71 | -7.55 | 0.16 | -1.51 | -1.32 | 0.19 |
| <i>cis-β</i> - 2BDP-F | -7.53 | -7.29 | 0.24 | -1.41 | -1.28 | 0.13 |
| <i>dis-cis-β</i> - 2BDP-F | -7.44 | -7.39 | 0.05 | -1.25 | -1.22 | 0.03 |

Table S7. MOs energies for dyads calculated in toluene using ω b97xd 6-31G*. CPCM model was used for solvent. Computations were performed on Spartan 10 for Windows (Wavefunction Inc, Irvine, CA).

| Dyad | HOMO-1 | HOMO | $\Delta(\text{HOMO})$ | LUMO | LUMO+1 | $\Delta(\text{LUMO})$ |
|------------------------------|---|---|-----------------------|---|---|-----------------------|
| β -2BDP-M |  -7.57 |  -7.14 | 0.43 |  -1.38 |  -1.07 | 0.31 |
| <i>dis</i> - β -2BDP-M |  -7.42 |  -7.02 | 0.40 |  -1.16 |  -0.87 | 0.29 |
| β -2BDP-B |  -7.43 |  -7.23 | 0.20 |  -1.24 |  -1.17 | 0.07 |

| | | | | | | |
|----------------------------------|--|--|------|--|--|------|
| <i>dis</i> - β - 2BDP-B |  -7.47 |  -7.31 | 0.16 |  -1.24 |  -1.18 | 0.06 |
| β - 2BDP-X |  -7.25 |  -7.01 | 0.24 |  -1.23 |  -1.05 | 0.18 |
| <i>dis</i> - β - 2BDP-X |  -7.49 |  -7.35 | 0.14 |  -1.28 |  -1.11 | 0.17 |
| <i>cis</i> - β - 2BDP-F |  -7.35 |  -7.07 | 0.28 |  -1.19 |  -1.07 | 0.12 |



S8. Structures of “disconnected” dyads.

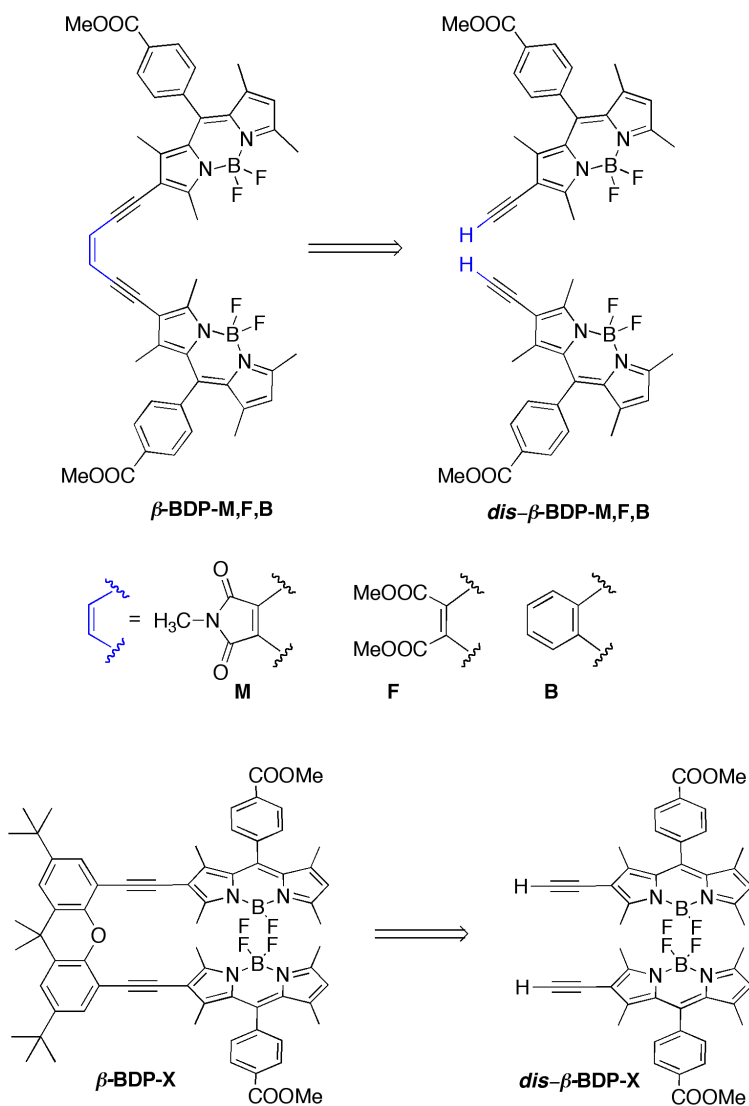


Figure S9. Structures of “disconnected” dyads discussed in the paper. These fictional dyads were created for computational purposes, by removing the entire linker except acetylene part, and substituting removed part by hydrogen. The distance and the mutual orientation of BODIPY subunits are the same as in the corresponding covalently-linked dyads.