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Supporting Information

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Density Functional Study of Tetraphenylporphyrin Long-Range Exciton Coupling

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The following information is provided in this document: optimized TPP geometry, dimer model geometry, and MM data for idealized dimer geometries. The geometries are given in xyz format for a Cartesian coordinate system (in Å).

TPP Optimized Geometry

78

C -2.429075 2.455719 0.036265
C -2.881253 1.133985 0.129199
C -1.082394 2.851624 -0.051896
C -4.232999 0.693570 0.307541
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C -2.884750 -1.125671 0.138065
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C 0.685866 4.233842 -0.257709
C 1.090878 2.849137 -0.042108
N -2.104773 0.002644 0.047716
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C -1.090878 -2.849137 -0.042108
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H 1.339087 -5.078531 -0.431976
C 2.436232 2.449442 0.052202
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C 4.232999 -0.693570 0.307541
C 2.881253 -1.133985 0.129199

N 2.104773 -0.002644 0.047716
H 5.082795 -1.358034 0.442085
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C 2.884750 1.125671 0.138065
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H 1.082801 -0.000841 -0.026302
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C 3.571450 4.412247 1.117903
C 5.348128 4.621345 -1.023451
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C 5.429836 5.523495 0.039752
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H -6.036251 -4.705243 -1.867496
H -4.602098 -6.115377 1.947483
H -6.186890 -6.311007 0.033329

TPP Dimer Geometry

156

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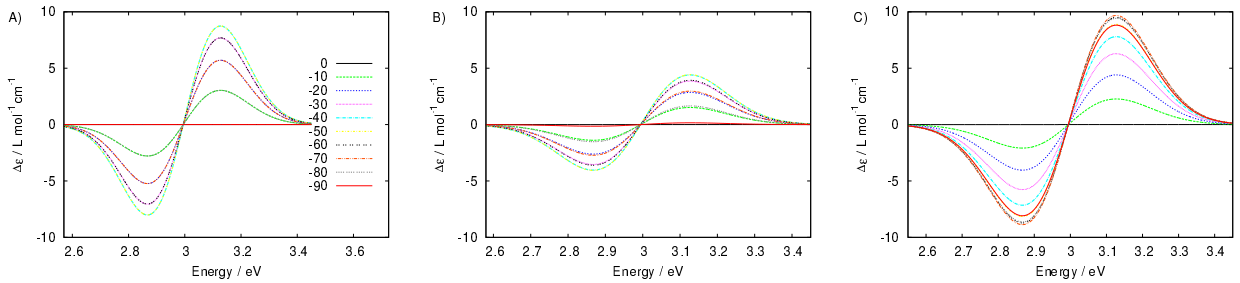

Figure S1: 2x2 matrix method coupling of B_x transitions for three sets of α angles (left to right, see text), with $\beta = 0°$ to $\beta = –90°$.

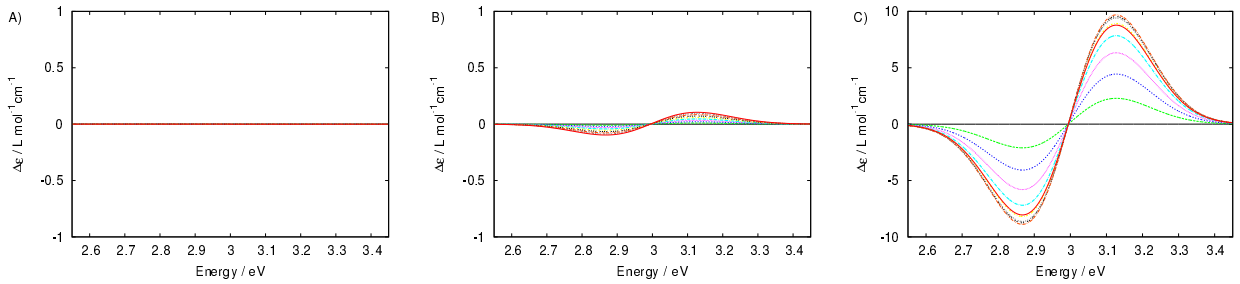

Figure S2: 4x4 matrix method coupling of degenerate $B_{x,y}$ transitions for three sets of α angles (left to right, see text) for $\beta = 0°$ to $\beta = –90°$.

Matrix Method (MM) calculations for an idealized TPP dimer geometry

Consider idealized TPP dimer geometries as discussed in Section 3.3 of the main article, with r_{ab} = 42Å. The system are explored for $\beta = 0$ going to $\beta = -90°$, in 10° intervals, for three cases: coupling of B_x only (one per monomer, Figure S1), coupling of degenerate B_x and B_y (Figure S2), and coupling of non-degenerate B_x/B_y transitions (Figure S3). For the degenerate case we set the excitation energy for $B_y = B_x$ and $d_y = d_x$ (vector magnitudes are in the y and x directions, respectively). The resulting CD spectra are plotted for $\alpha_a = \alpha_b$ = 90° (A), α_a = 90° / α_b = 45° (B), and α_a = 135° / α_b = 45° (C) for changing β. The x direction has been shosen to coincide with the transition dipole orientations for $\alpha = 90°$ (see Figure 10 in main article). In Figure S1A, the key is representative of all plots; the printed value represents the β angle. $E_{a/b}$ was set to 3.0 eV for the 2x2 and the degenerate 4x4 cases, while E_b was increased by 0.1 eV for the non-degenerate cases. The $d_{x/y}$ magnitude was set to 3.0 a.u. for all spectra.

In Figure S1 the 2x2 matrix problem yields the predicted CD sign pattern. For $\alpha_a = \alpha_b = 90°$ the plots are symmetric about $\beta = -45°$ due to the $\sin\beta$ term in $R_{1/2}$ (Equation 7a). In Figure S2, the 4x4 matrix problem is more complicated. For $\alpha_a = \alpha_b = 90°$ no net CD intensity is obtained for any value of β because of exact cancellation of the calculated rotatory strengths. In the 4x4 case with $\alpha_a = 90°$ and $\alpha_b = 45°$ the calculated CD has low intensity. When $\alpha_a = 135°$, the CD intensity reaches the same magnitude as the CD obtained from coupling one transition per

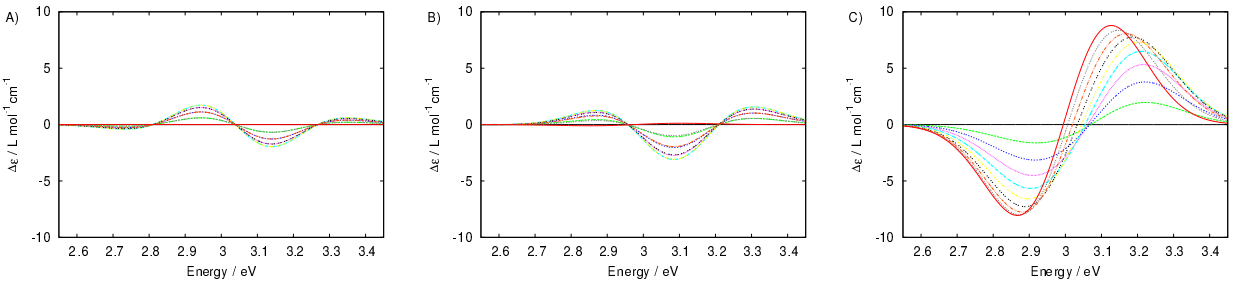

Figure S3: 4x4 matrix method coupling for non-degenerate $B_{x,y}$ transitionsfor three sets of α angles (left to right, see text) for $\beta = 0°$ to $\beta = –90°$.

monomer (Figure S1). When the transitions are non-degenerate the picture becomes comparable to the case observed in the article. When the α terms are 90° the spectrum is split into two weak negative CD couplets centered at 2.8 and 3.3 eV respectively. When $\alpha_b = 45°$ a spectrum emerges where the negative peak at higher energy dominates the spectrum. In system C, with $\alpha_a = 135°$, as β approaches –90° the dipole interaction potential for the B_y transitions becomes very small, and therefore the CD couplet is dominated by interaction of the B_x transitions only, leading to a negative CD couplet centered at 3 eV, with an intensity comparable to that seen in Figures S1 and S2.