

Robustness, efficiency and optimality in the Fenna-Matthews-Olson photosynthetic pigment-protein complex: Supplementary Information

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I. ELECTRONIC HAMILTONIAN FOR FENNA-MATTHEWS-OLSON COMPLEX

Written in the basis of molecular excited states, such that $H_{ex}(i, j) = \langle i | \hat{H}_{ex} | j \rangle$, the electronic sub-system Hamiltonian for the Fenna-Matthews-Olson (FMO) complex considered here is^{1,2}

$$H_{ex} = \begin{pmatrix} 310.0 & -97.9 & 5.5 & -5.8 & 6.7 & -12.1 & -10.3 & 37.5 \\ -97.9 & 230.0 & 30.1 & 7.3 & 2.0 & 11.5 & 4.8 & 7.9 \\ 5.5 & 30.1 & 0.0 & -58.8 & -1.5 & -9.6 & 4.7 & 1.5 \\ -5.8 & 7.3 & -58.8 & 180.0 & -64.9 & -17.4 & -64.4 & -1.7 \\ 6.7 & 2.0 & -1.5 & -64.9 & 405.0 & 89.0 & -6.4 & 4.5 \\ -12.1 & 11.5 & -9.6 & -17.4 & 89.0 & 320.0 & 31.7 & -9.7 \\ -10.3 & 4.8 & 4.7 & -64.4 & -6.4 & 31.7 & 270.0 & -11.4 \\ 37.5 & 7.9 & 1.5 & -1.7 & 4.5 & -9.7 & -11.4 & 505.0 \end{pmatrix}. \quad (1)$$

The standard deviations in the off-diagonal elements were determined as the mean difference in coupling strengths from different green sulfur bacteria species (*C. tepidum* and *P. aestuarii*),¹ giving an average value of 3.5 cm^{-1} . The standard deviations in the site energies were determined by empirical analysis of FMO optical spectra,³ specifically, the values were $\sigma_1 = \sigma_3 = \sigma_4 = 25.5 \text{ cm}^{-1}$, $\sigma_2 = 42.5 \text{ cm}^{-1}$, $\sigma_5 = \sigma_6 = \sigma_7 = \sigma_8 = 51.0 \text{ cm}^{-1}$. Note that, because the previous work studied the seven-site FMO model, we have assumed that $\sigma_8 = 51.0 \text{ cm}^{-1}$. These standard deviation values were used to generate new FMO-like Hamiltonians to assess the impact of network changes on the excitation energy transport (EET) efficiency.

II. EFFECT OF COUPLING REMOVAL ON EET EFFICIENCY

In the main manuscript, we show the effects of removing different Bchl sites on the EET efficiency. This “knockout” study can be extended to include the removal of off-diagonal elements from the FMO electronic Hamiltonian, corresponding to removal of vertices from the network; the results for calculated efficiencies in these cases can be used to infer the identities of Bchl sites which sit along the most important EET pathways. Figures 1, 2 and

3 show the results of removing two vertices from the FMO Hamiltonian.

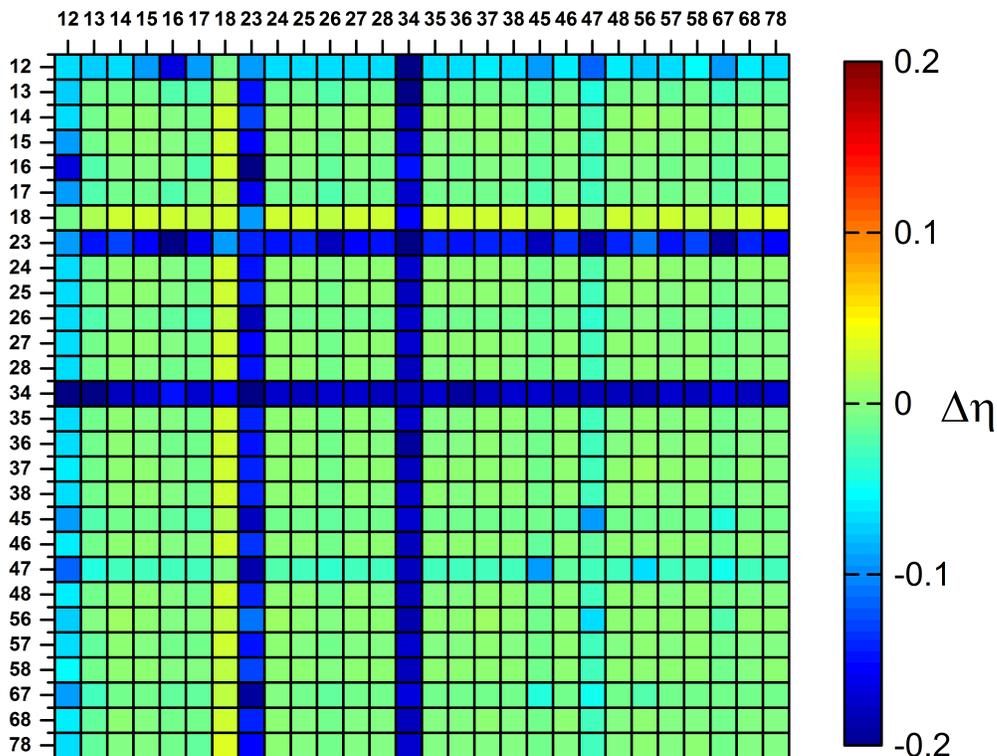


FIG. 1: EET efficiency calculated for FMO Hamiltonians in which increasing two off-diagonal coupling elements are removed. The axes indicate the off-diagonal elements being removed, such that the entry (12,45) corresponds to an EET efficiency calculation in which elements $H_{ex}(1,2)$ and $H_{ex}(4,5)$ (as well as $H_{ex}(2,1)$ and $H_{ex}(5,4)$) have been set to zero. The colour of the corresponding cell indicates the change in EET efficiency relative to the original FMO model. This Figure was determined for initial excitation at Bchl 1, and can be used to infer the existence of important EET paths. For example, removing couplings $H_{ex}(1,2)$ and $H_{ex}(3,4)$ shuts down transport amongst two major pathways from Bchl 1 to Bchl 3, as can be inferred from the strongly negative change in EET efficiency.

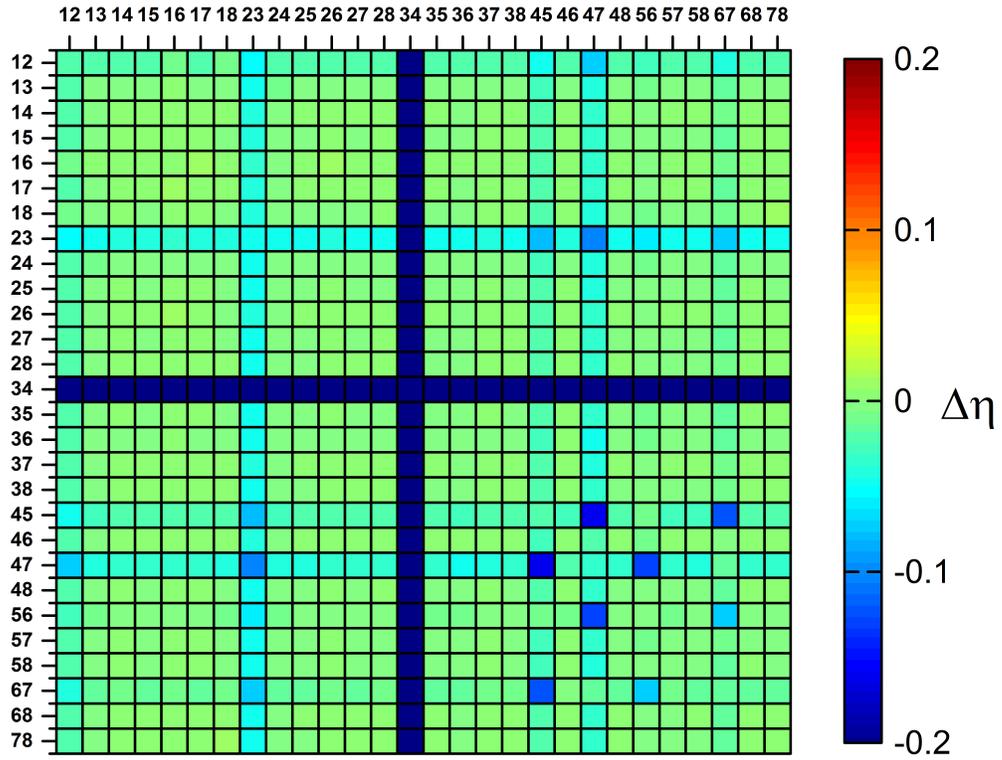


FIG. 2: As Fig. 1, but for initial excitation at Bchl 6.

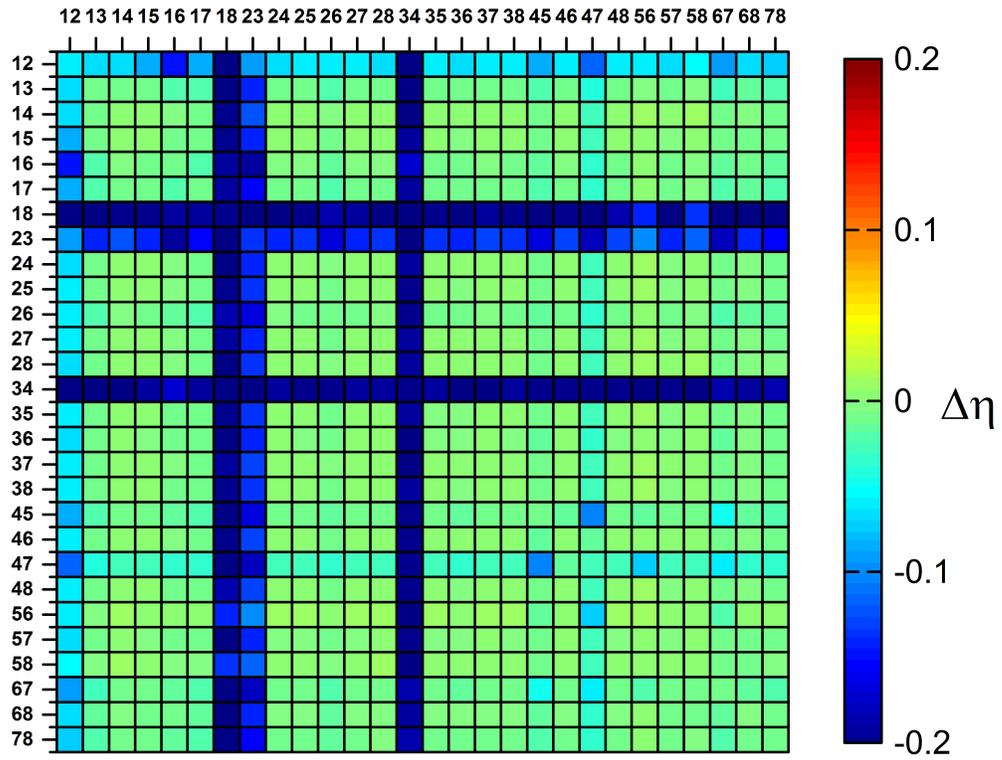


FIG. 3: As Fig. 1, but for initial excitation at Bchl 8.

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