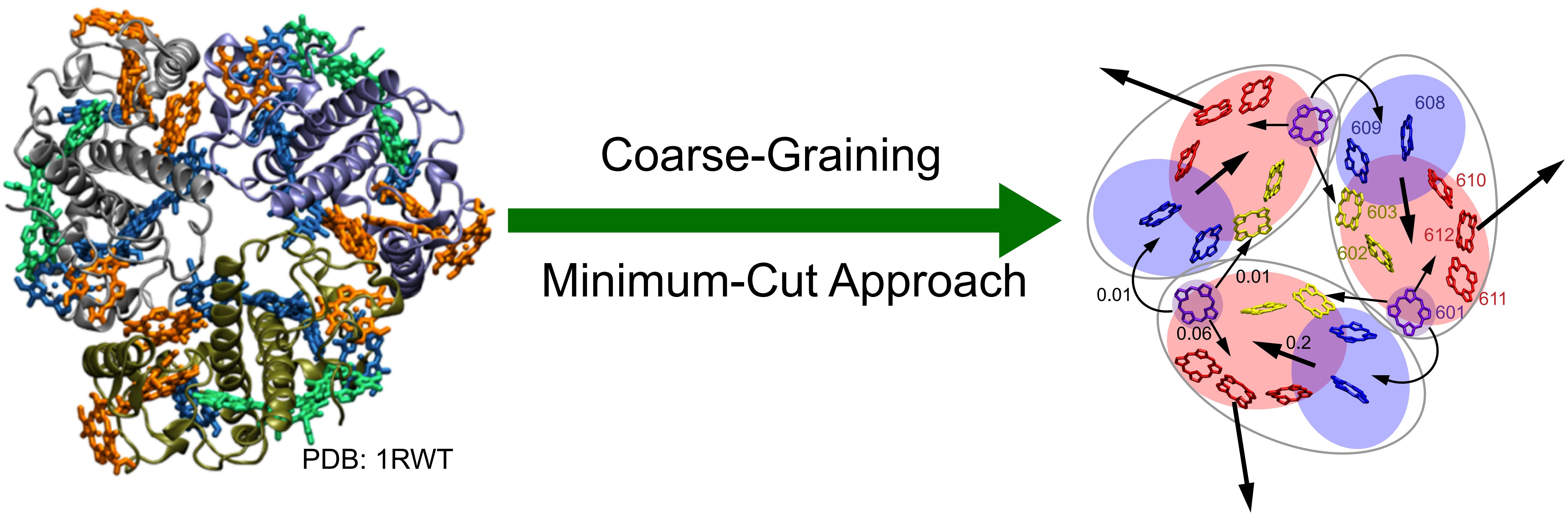
Understanding Complex Excitation Energy Transfer Networks with a Systematic Approach



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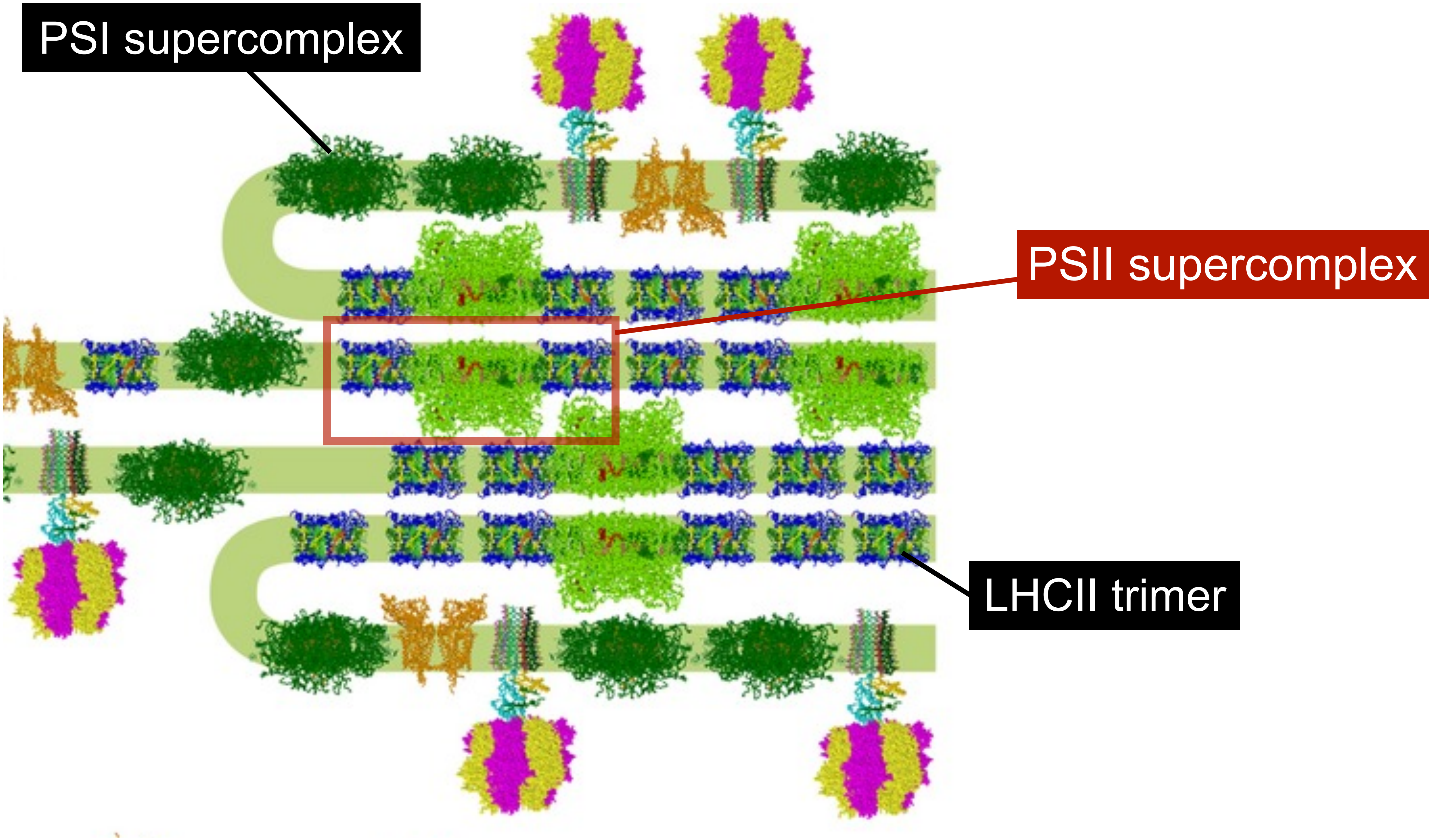
Outlines

- **Backgrounds and Reviews**
  - Excitation energy transfer (EET) networks
  - The minimum-cut approach
  - LHCII monomer
- Results:
  - LHCII trimer
  - Static Disorder Effects on LHCII

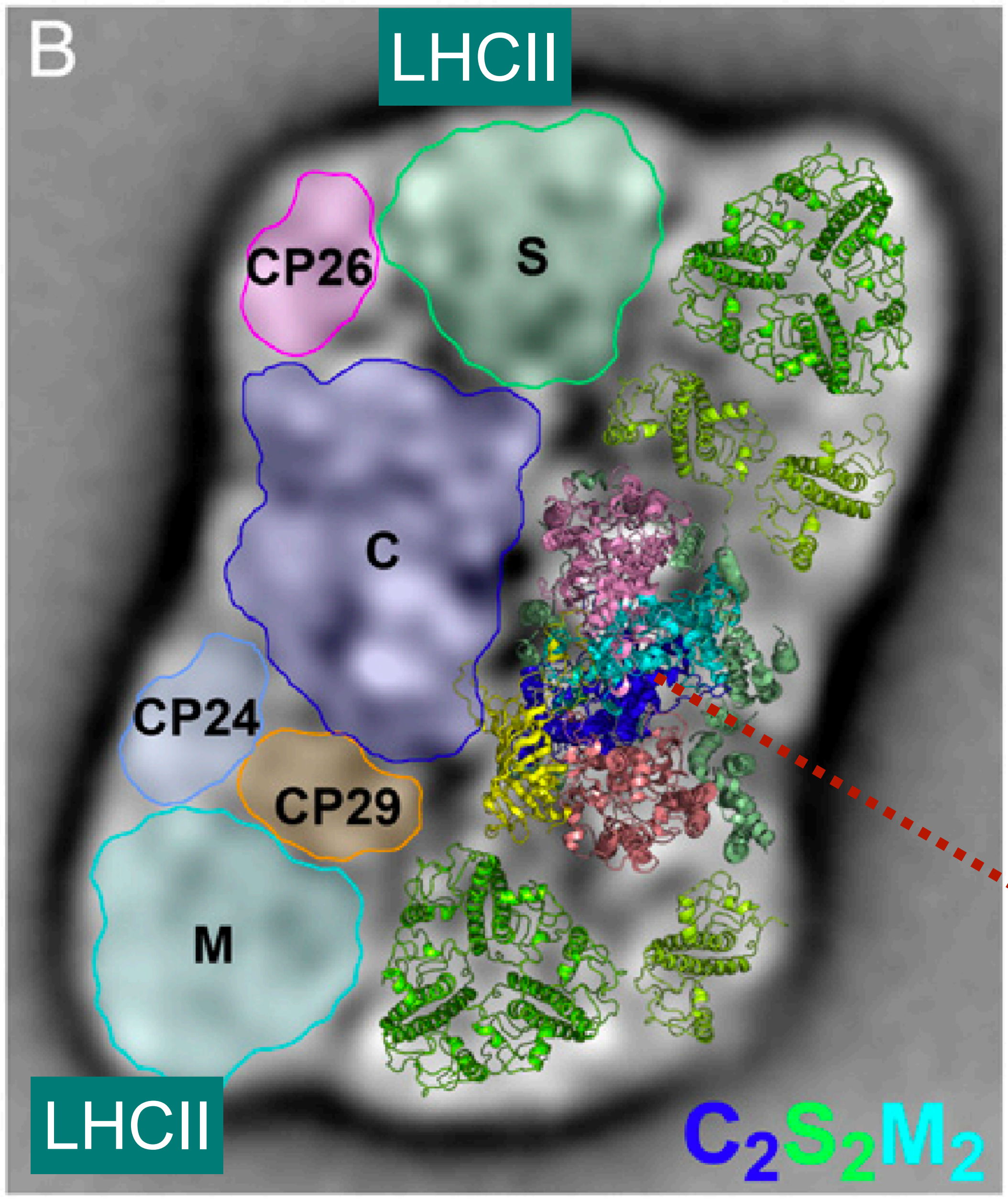
Thylakoid Membrane

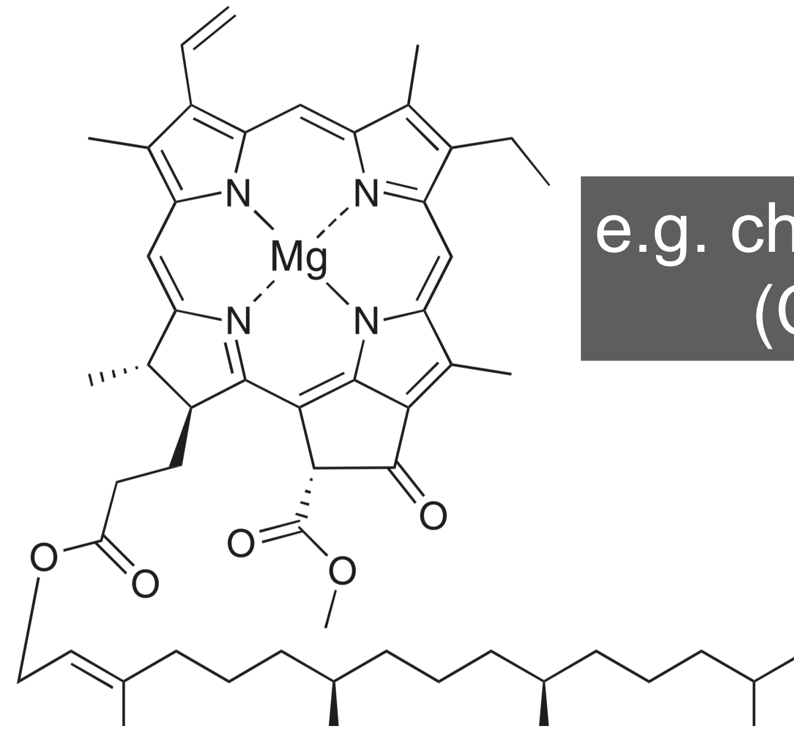


Minagawa, J. et al *Plant J.* **2015**, *82*, 413

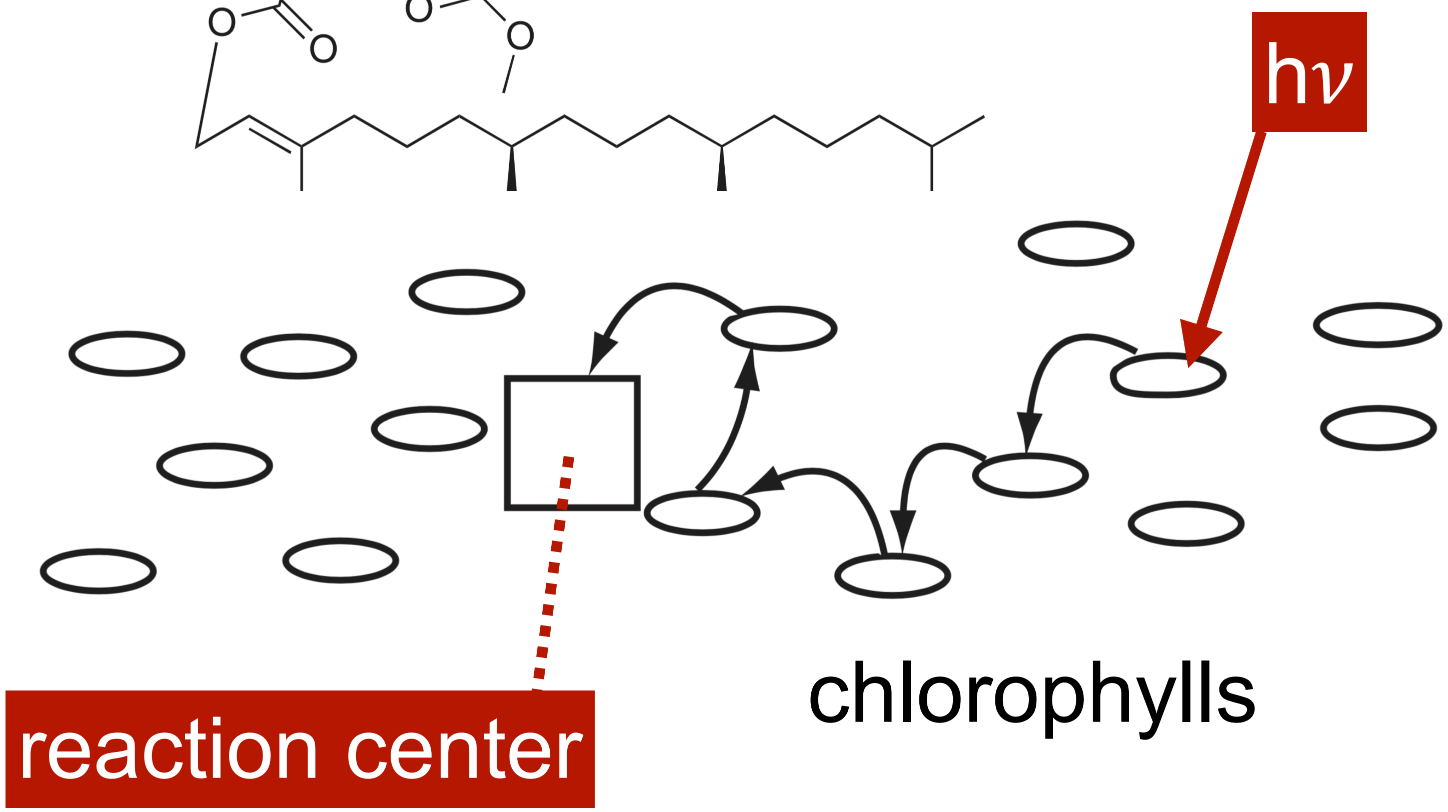
Excitation Energy Transfer (EET) Network

e.g. Photosystem II supercomplex:
hundreds of chlorophylls





e.g. chlorophyll *a*
(Chl *a*)

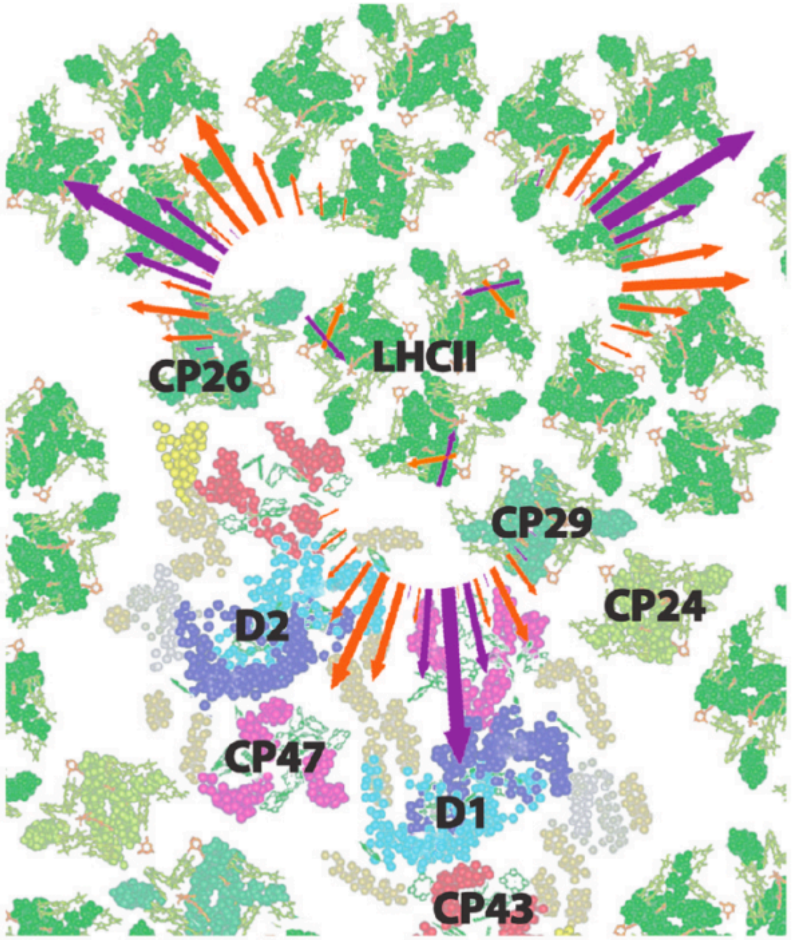


Extremely complicated chlorophyll network!

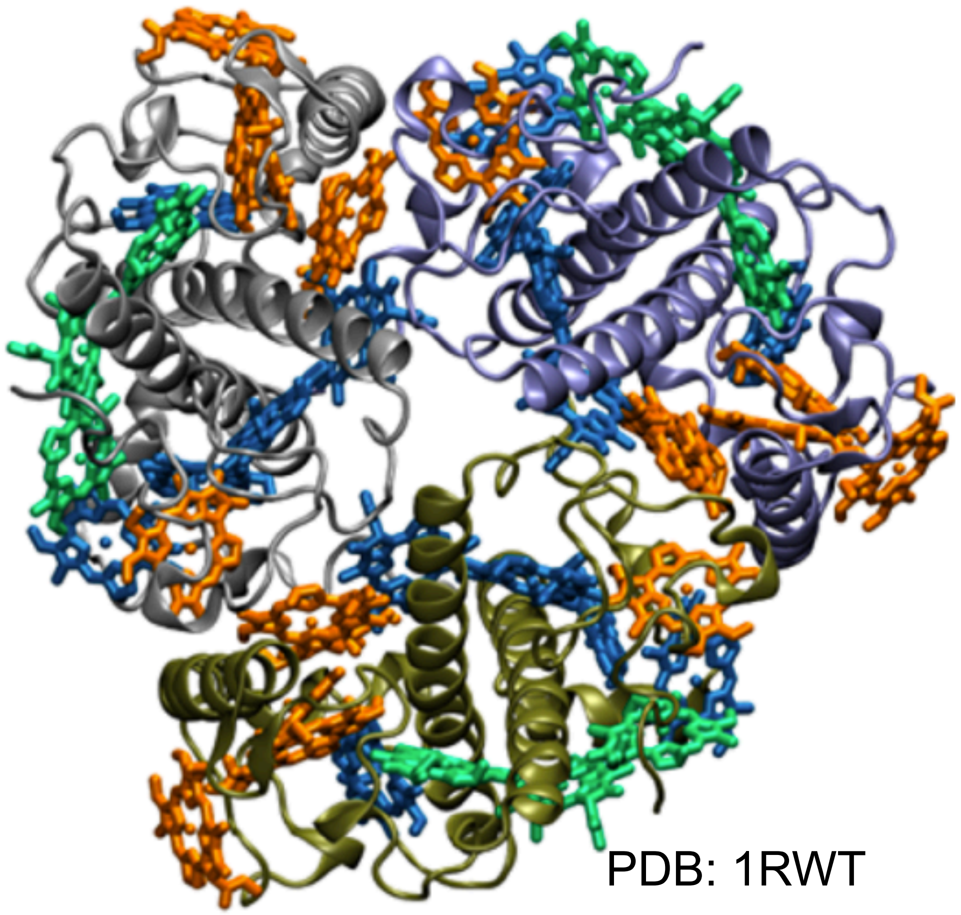
Kouřil, R. et al *Biochim. Biophys. Acta* **2012**, *1817*, 2
Blankenship, R. E. *Molecular Mechanisms of Photosynthesis* 2/e, Oxford, UK, **2014**

Light Harvesting Complex II (LHCII)

- Found in plants and many algae
- Mainly in trimer form
- 14 sites = 8 Chl *a* + 6 Chl *b*

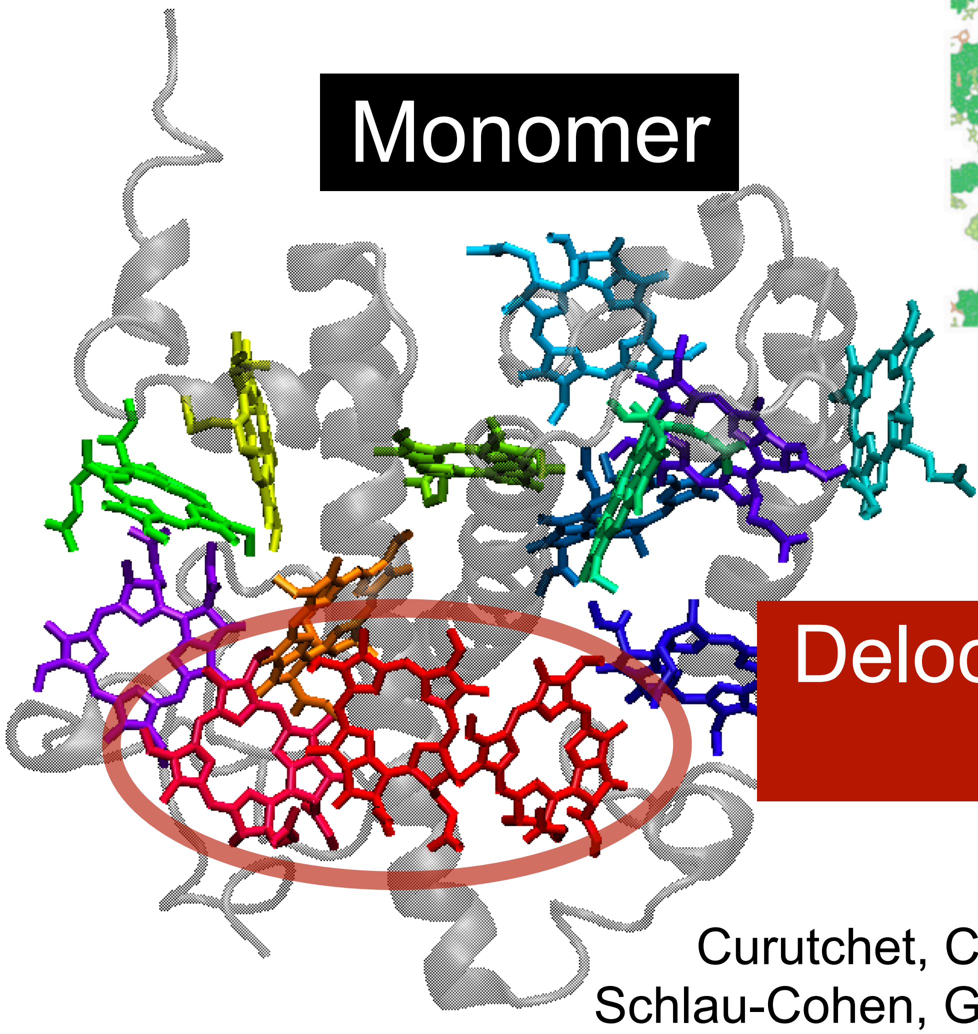


Trimer



PDB: 1RWT

Monomer



Delocalized lowest energy exciton state

Liu, Z. *Nature* **2004**, *428*, 287
Curutchet, C. *et al Chem. Rev.* **2017**, *117*, 294
Schlau-Cohen, G. S. et al *JPC B* **2009**, *113*, 15352

Modeling the EET Network

Effective Hamiltonian (Sites/Chls)

↓ **Basis Transform**

Frenkel Exciton Hamiltonian

$$H = H_e + H_{ph} + H_{e-ph}$$

$$H_e = \sum_i E_i |i\rangle\langle i|$$

$$H_{ph} = \sum_\nu \omega_\nu b_\nu^\dagger b_\nu$$

$$H_{e-ph} = \sum_{i,j} (H_{e-ph})_{ij} |i\rangle\langle j|$$

→ **Modified Redfield Theory** →

Rate Constant Matrix

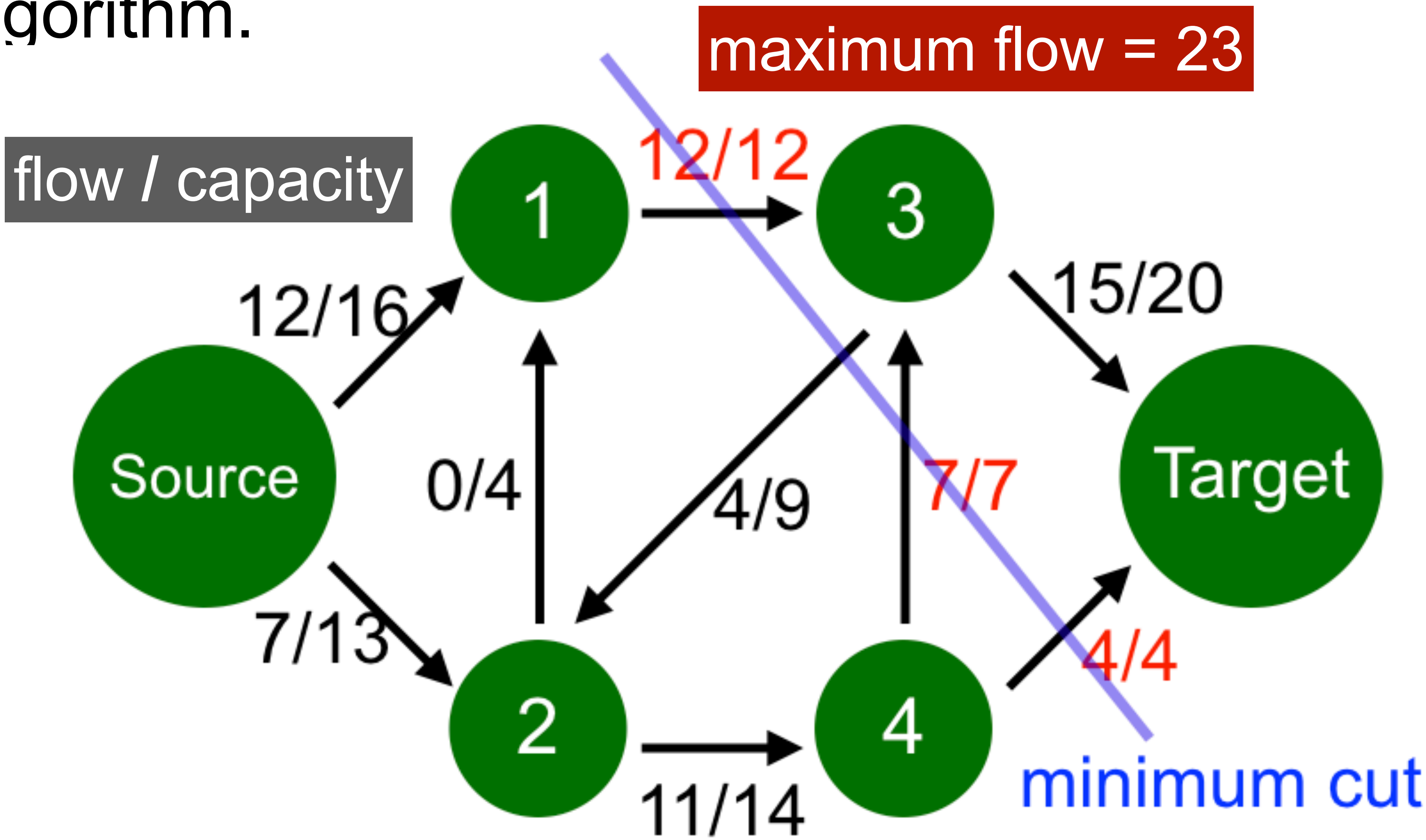
$$\mathbf{R} = \sum_{i \neq j} r_{ij} |i\rangle\langle i|$$

↑ **Adjacency Matrix**

Direct Graph

Minimum-Cut Problem

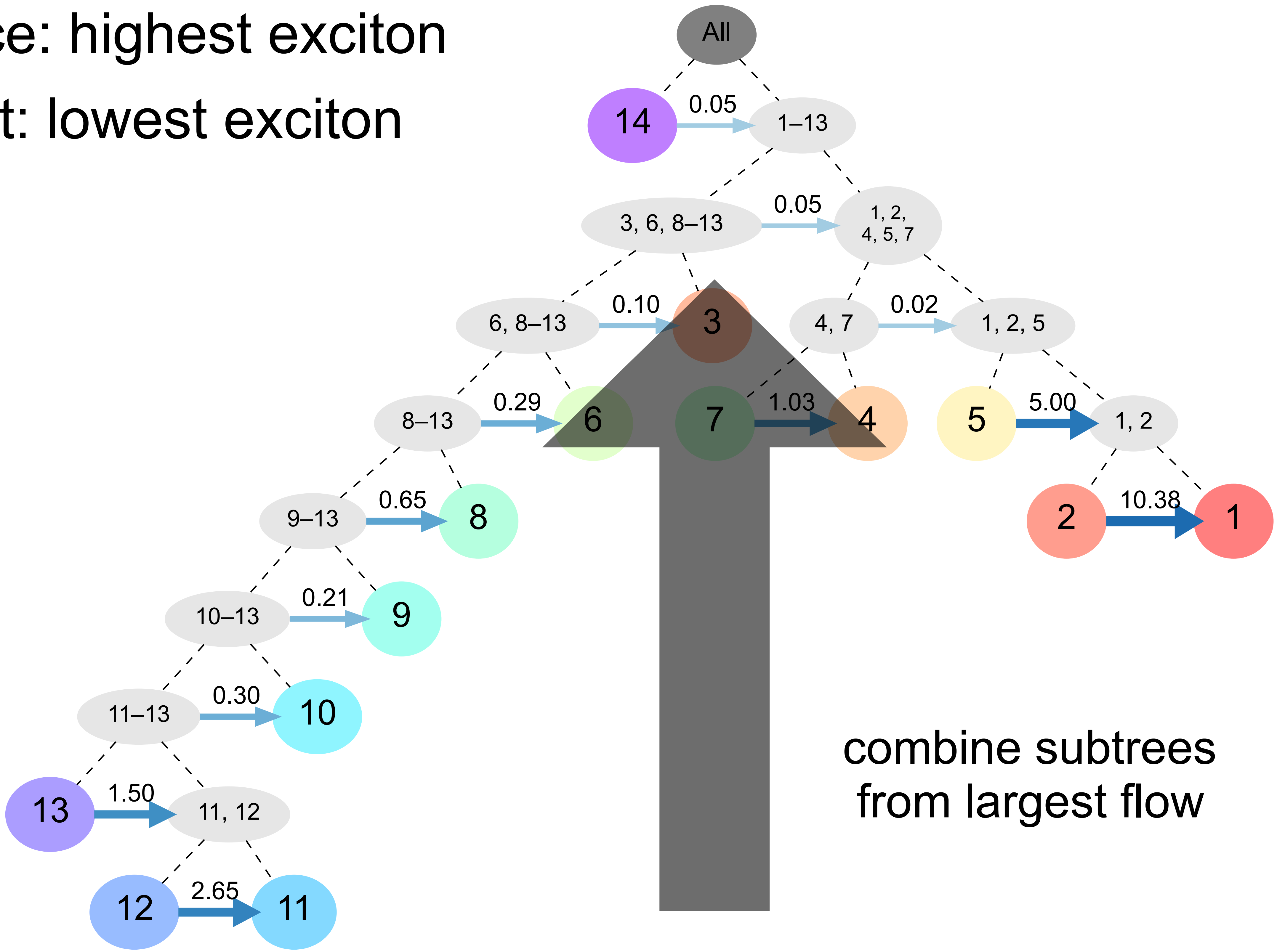
- To identify bottlenecks in energy transfer networks, we apply the minimum-cut methods with Ford-Fulkerson algorithm.



Ford, L. R.; Fulkerson, D. R. *Can. J. Math.* **1956**, *8*, 399

Minimum-Cut Approach

- Source: highest exciton
- Target: lowest exciton



Simulating EET

Reduced Rate Constants

$$r_{\mathrm{ST}} = \sum_{j \in \mathrm{T}} \sum_{i \in \mathrm{S}} r_{ij} \frac{\exp(-\beta E_i)}{Z_{\mathrm{S}}}$$

Population Dynamics

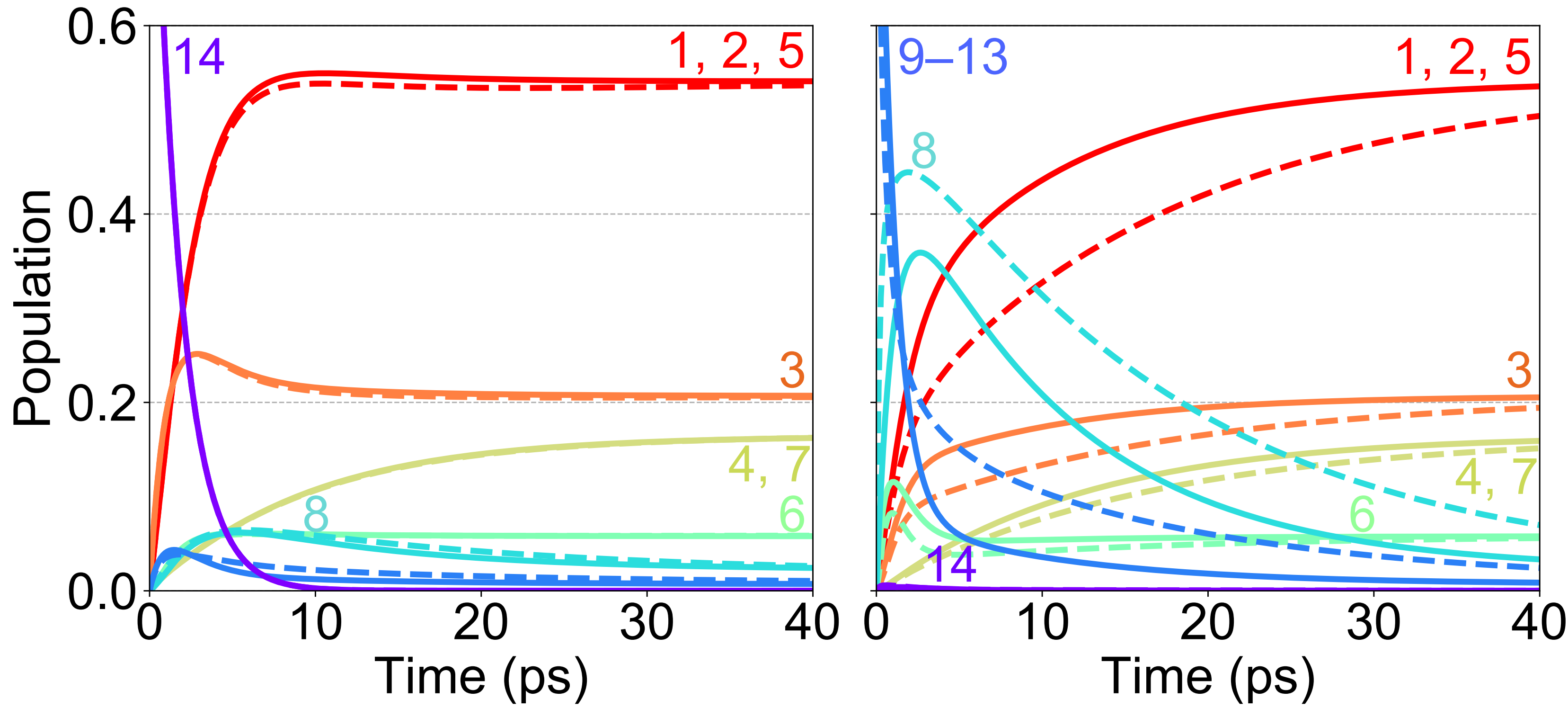
$$\frac{d}{dt} P(t) = \mathbf{R} P(t)$$

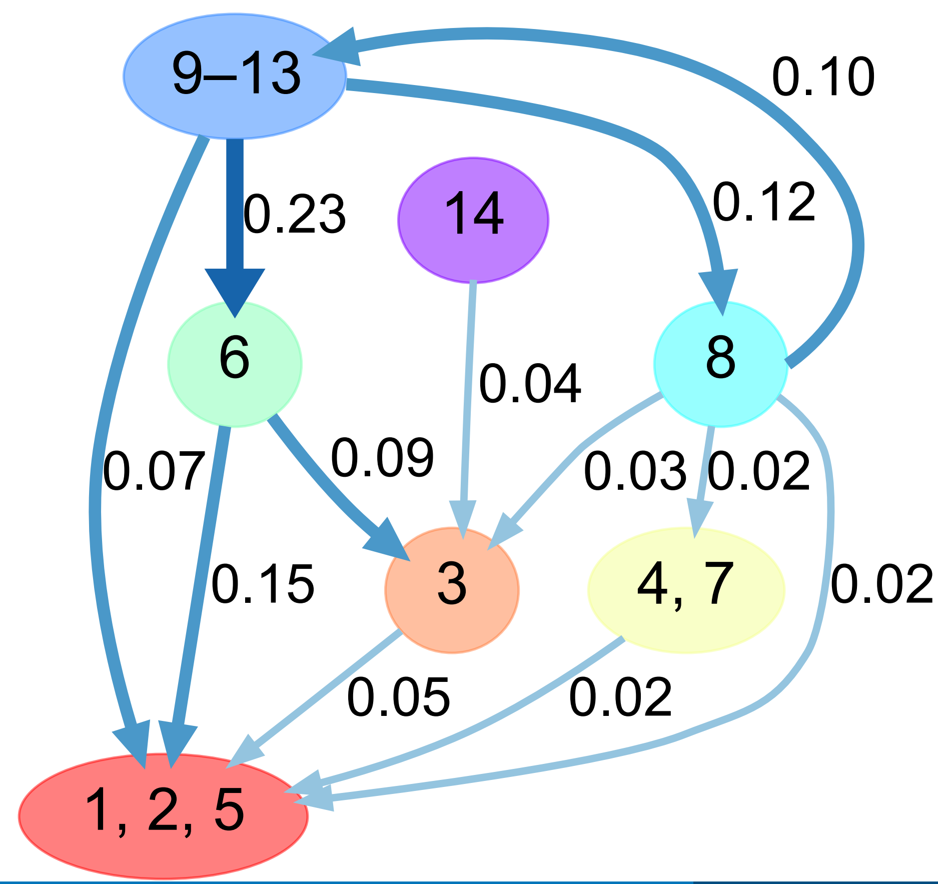
Time-Integrated Flux (Flow)

$$f_{ij}(t) = R_{ij} P_i(t) - R_{ji} P_j(t)$$

$$F_{ij} = \int_0^T f_{ij}(\tau) - f_{ij}(t \to \infty)\, d\tau$$

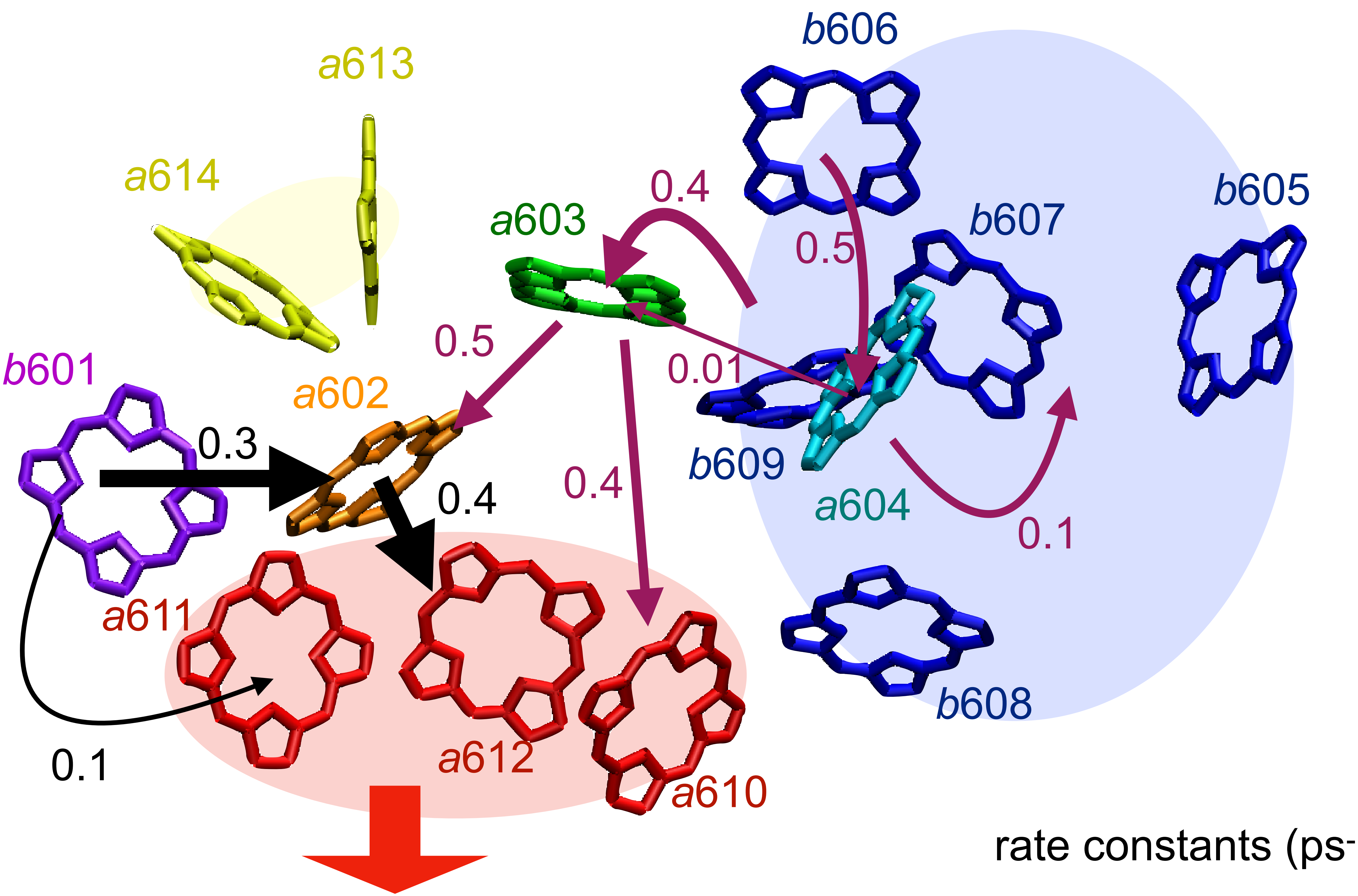
Wu, J. et al *JPCL* **2015**, *6*, 1240





T = 60 ps

EET Pathway of LHCII Monomer



rate constants (ps^{-1})

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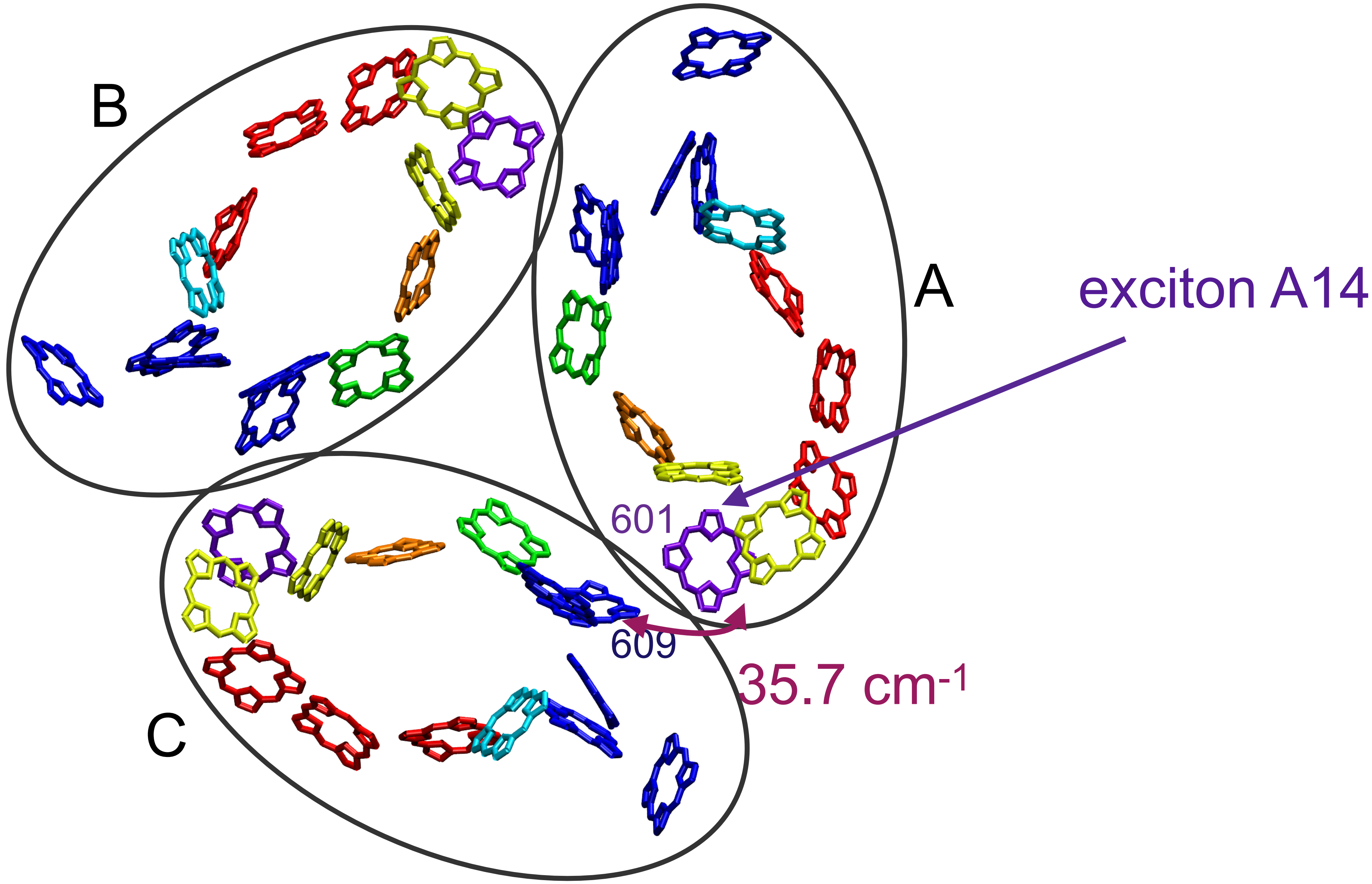
  - Static Disorder Effects on LHCII

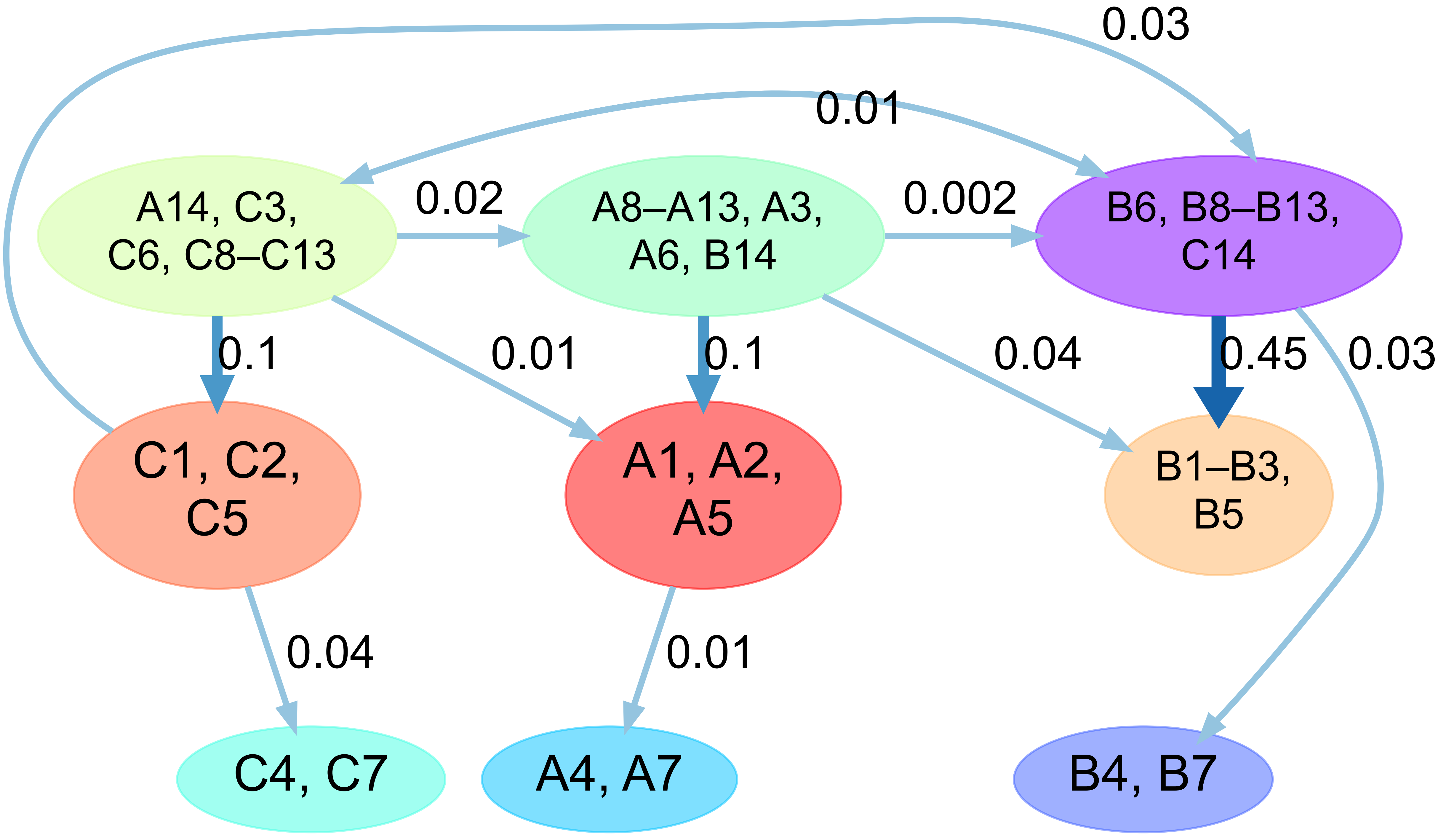
Model for LHCII Trimer

- 20 cm^{-1} random static disorders: prevent accidental degeneracies

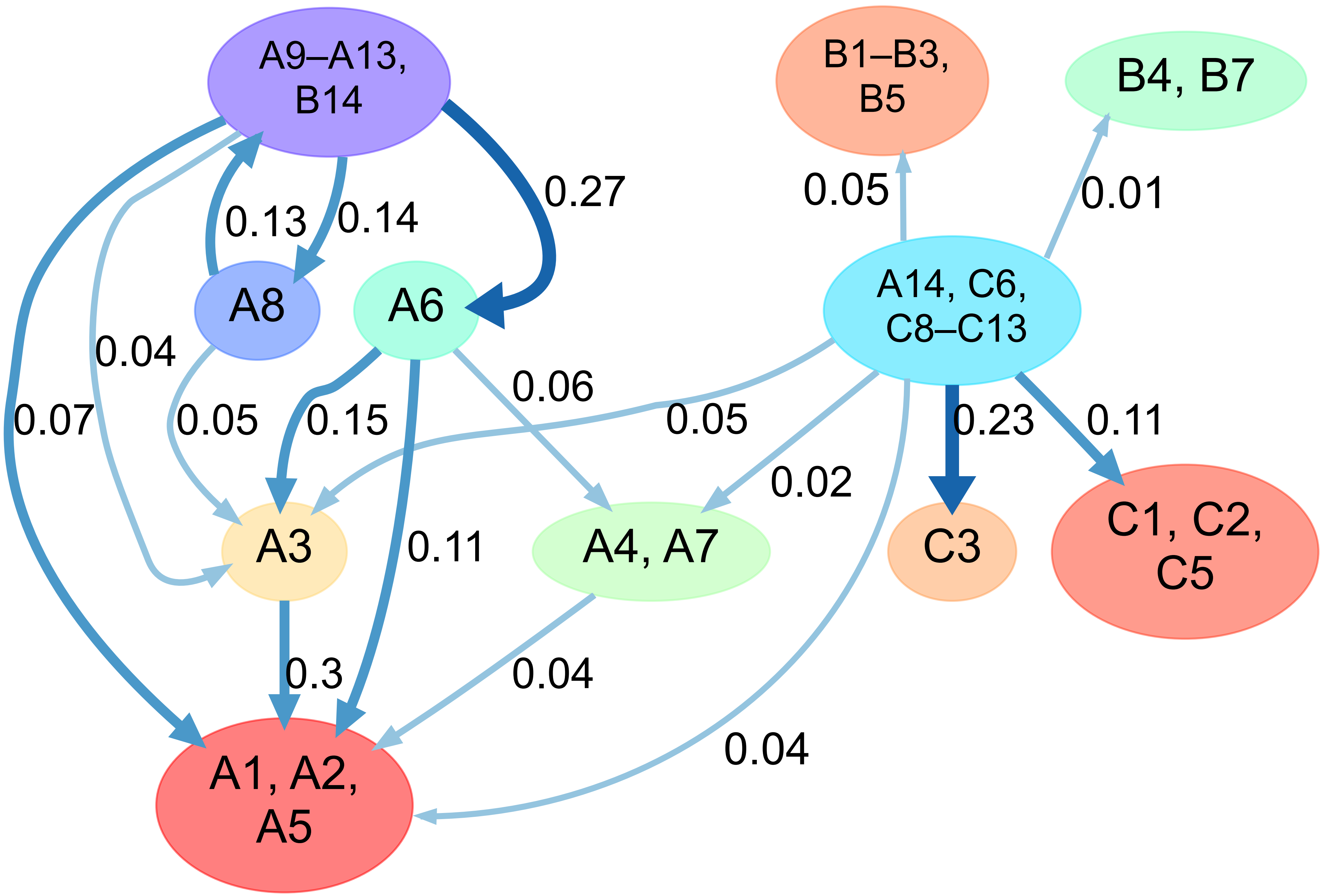


Frähmcke, J. S.; Walla, P. J. *Chem. Phys. Lett.* **2006**, *430*, 397

9-Cluster Model



15-Cluster Model



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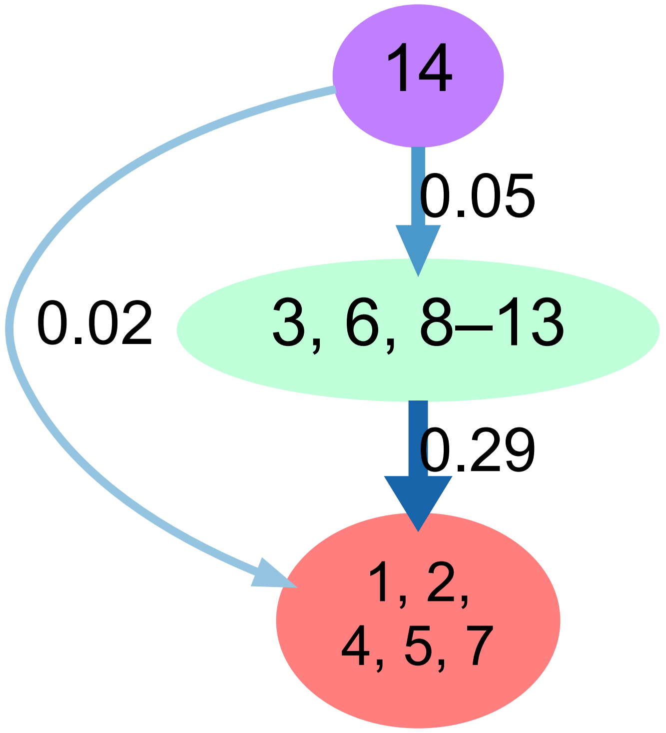
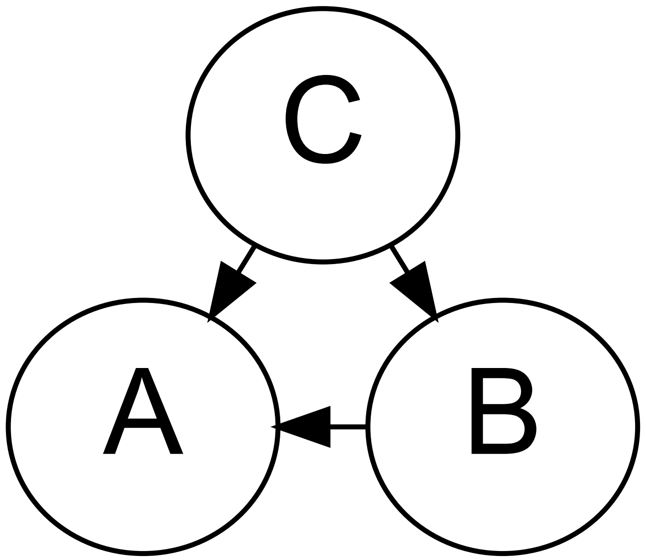
  - **Static Disorder Effects on LHCII**

Simulation of Static Disorders

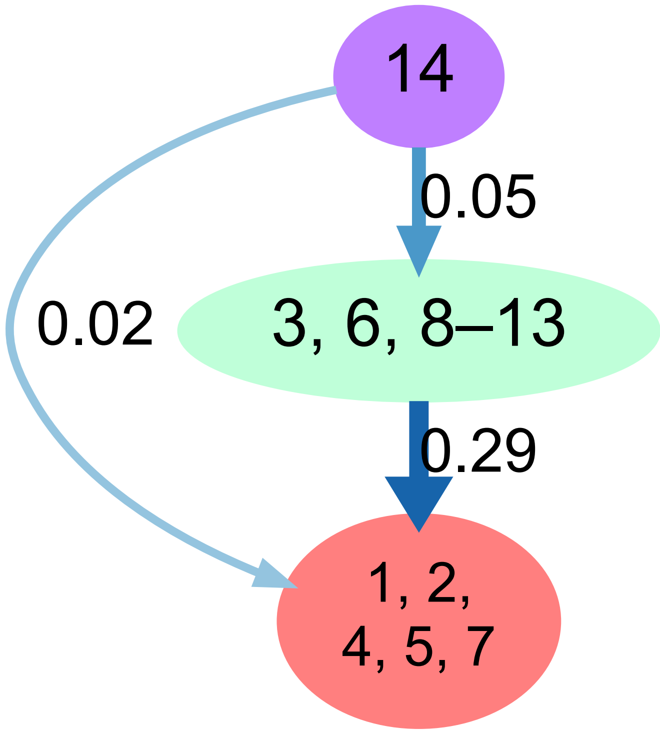
- LHCII monomer
- 100 cm^{-1} Gaussian random disorders
- Analyze the 3-cluster models
- Repeat 1000 times

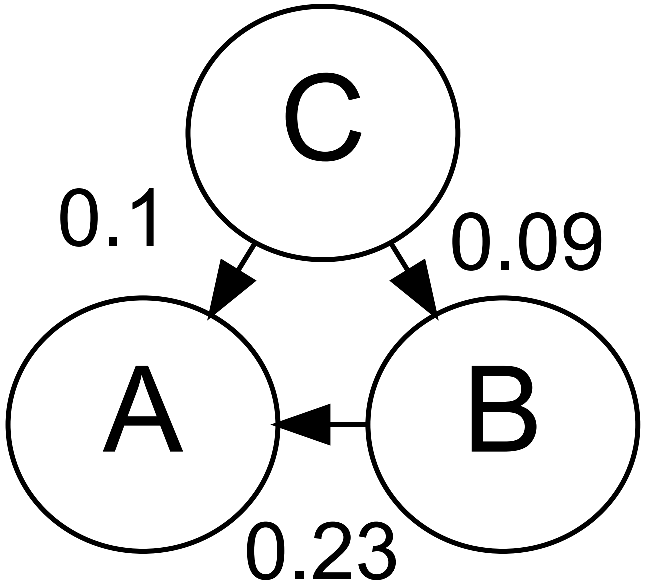


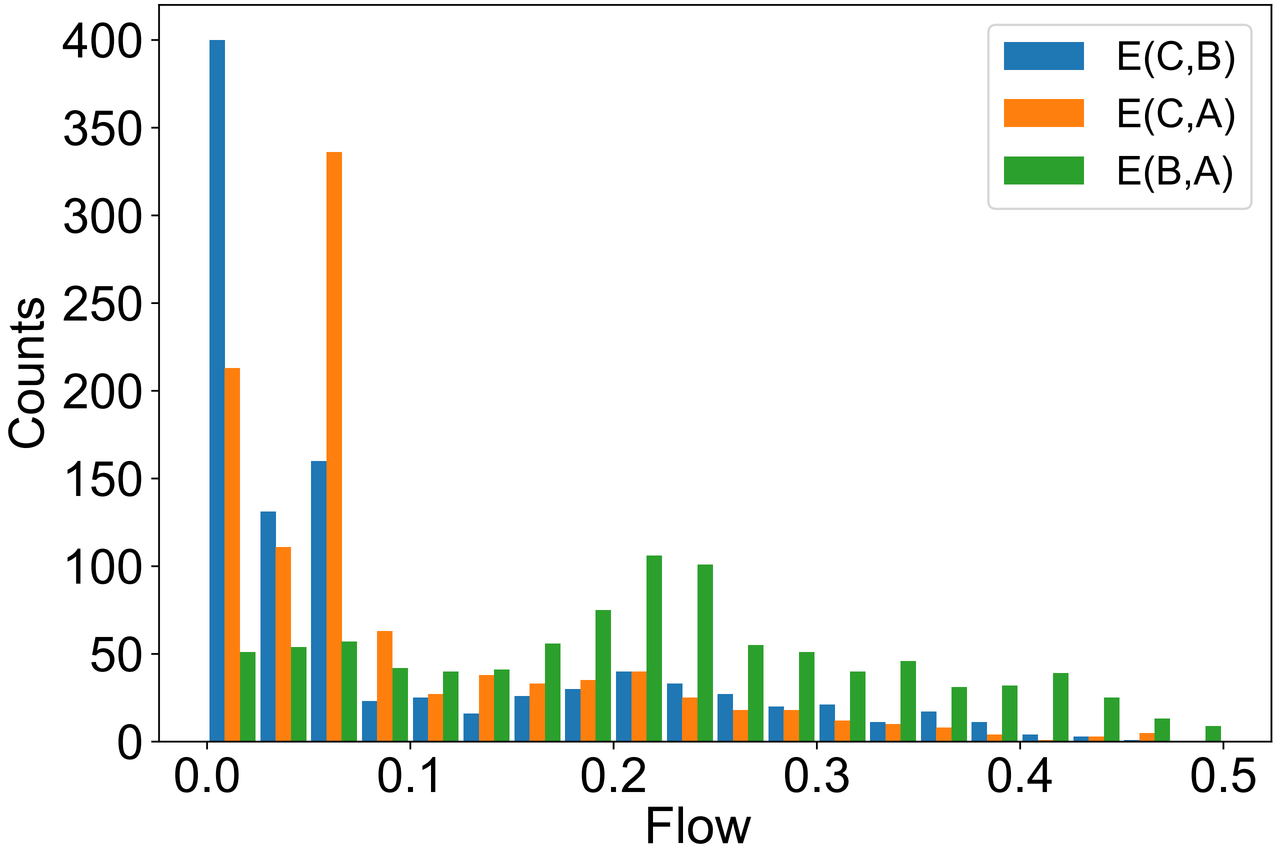
- Introduce a simple energy hierarchy



First Glance

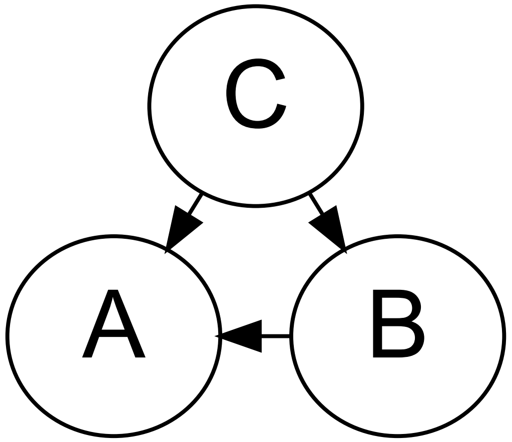




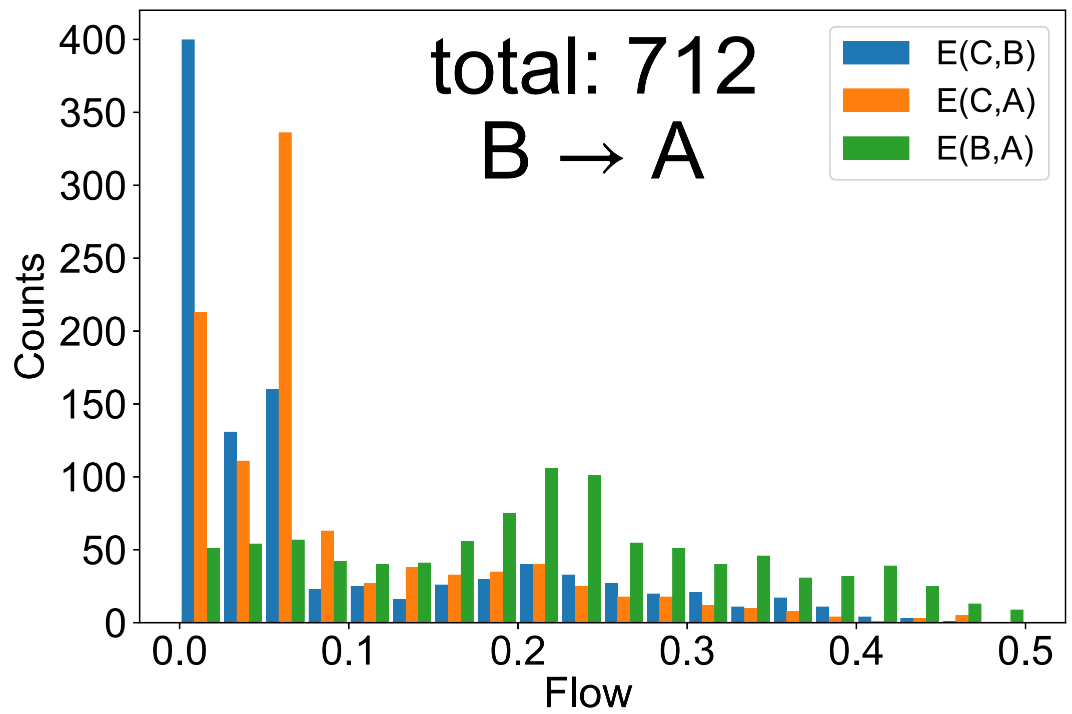


exciton	C_A	C_B	C_C	r_A	r_B	r_C
1	809	168	23	18%	4%	1%
2	797	165	38	17%	3%	0%
3	514	443	43	11%	13%	1%
4	469	342	189	7%	5%	2%
5	799	177	24	18%	5%	1%
6	373	403	224	5%	6%	3%
7	455	348	197	6%	5%	2%
8	42	600	358	1%	11%	6%
9	65	576	359	1%	10%	6%
10	42	591	367	1%	10%	6%
11	368	372	260	4%	4%	3%
12	395	368	237	5%	5%	3%
13	36	597	367	0%	11%	6%
14	119	204	677	6%	8%	60%

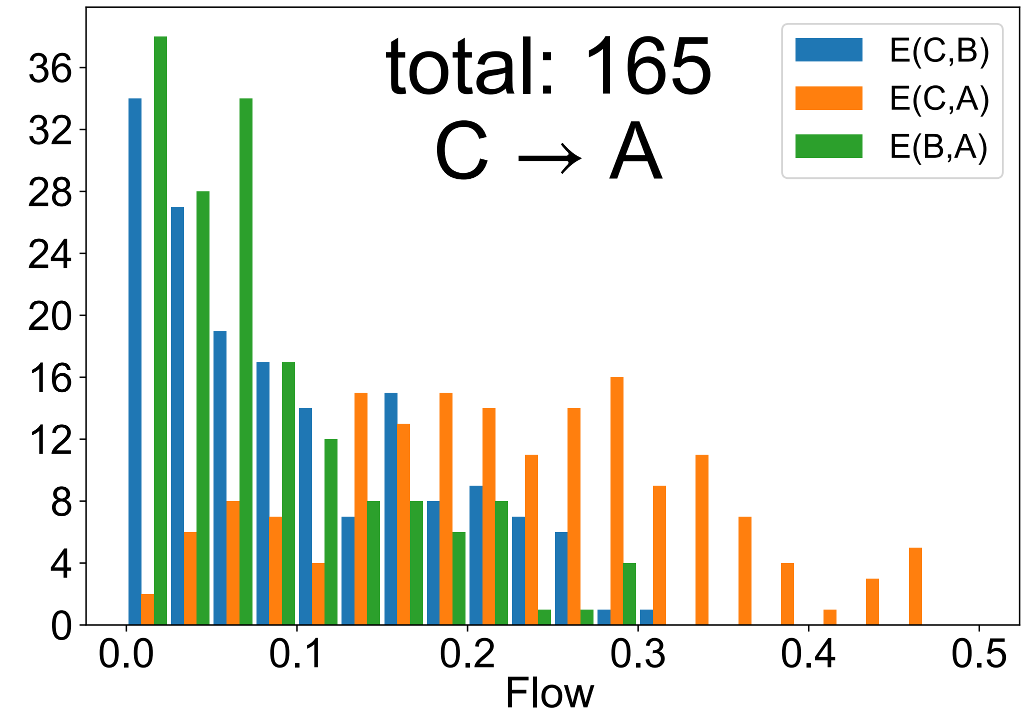
4 Classes



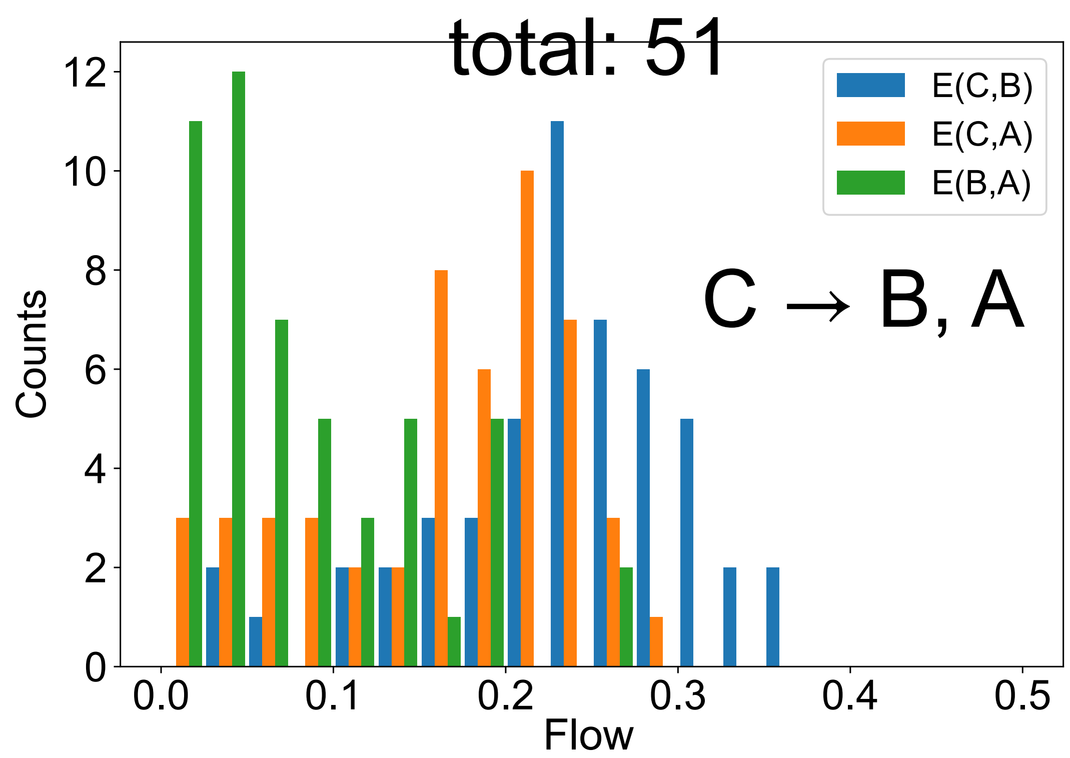
C
A
B



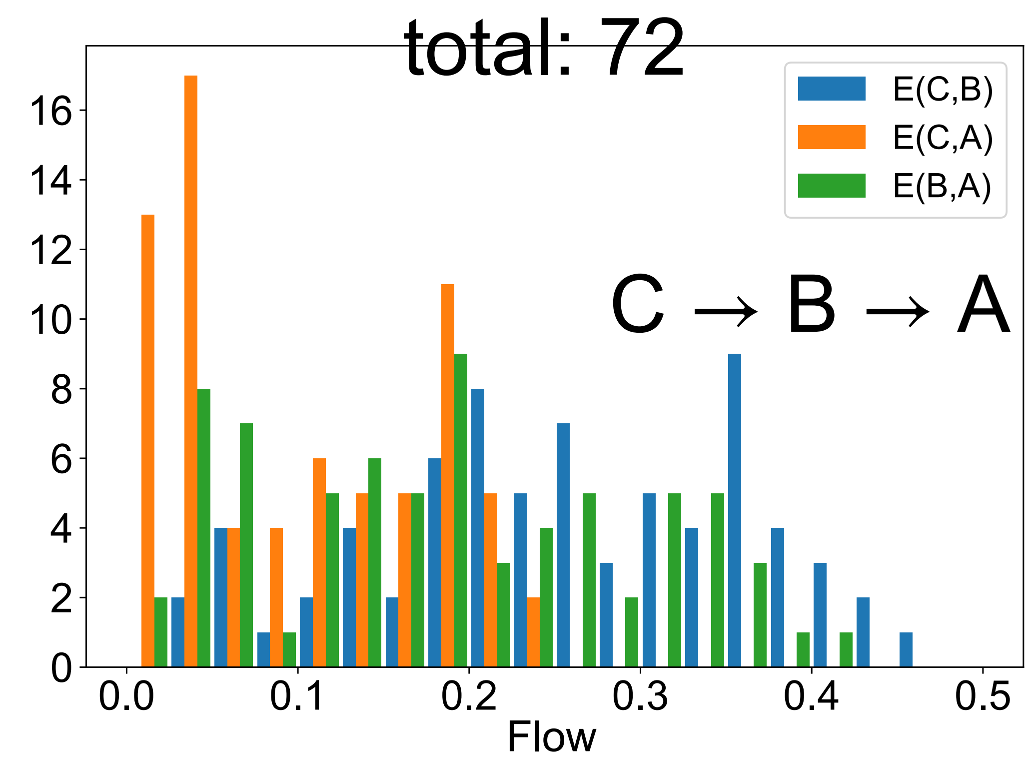
total: 712
B → A
E(C,B)
E(C,A)
E(B,A)
Counts
Flow



total: 165
C → A
E(C,B)
E(C,A)
E(B,A)
Flow

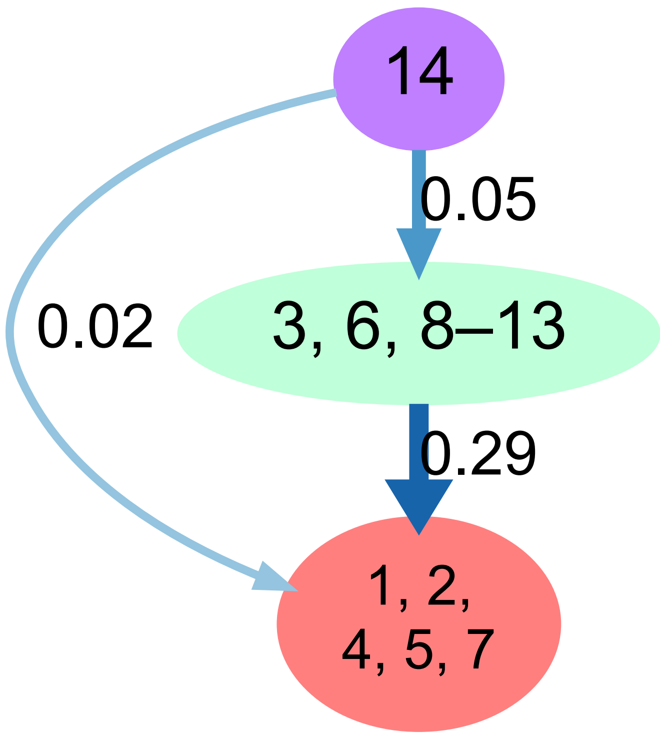


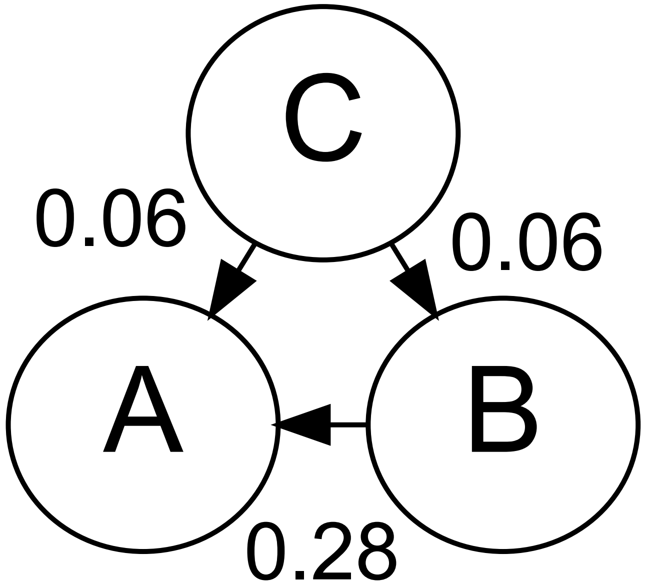
total: 51
C → B, A
E(C,B)
E(C,A)
E(B,A)
Counts
Flow

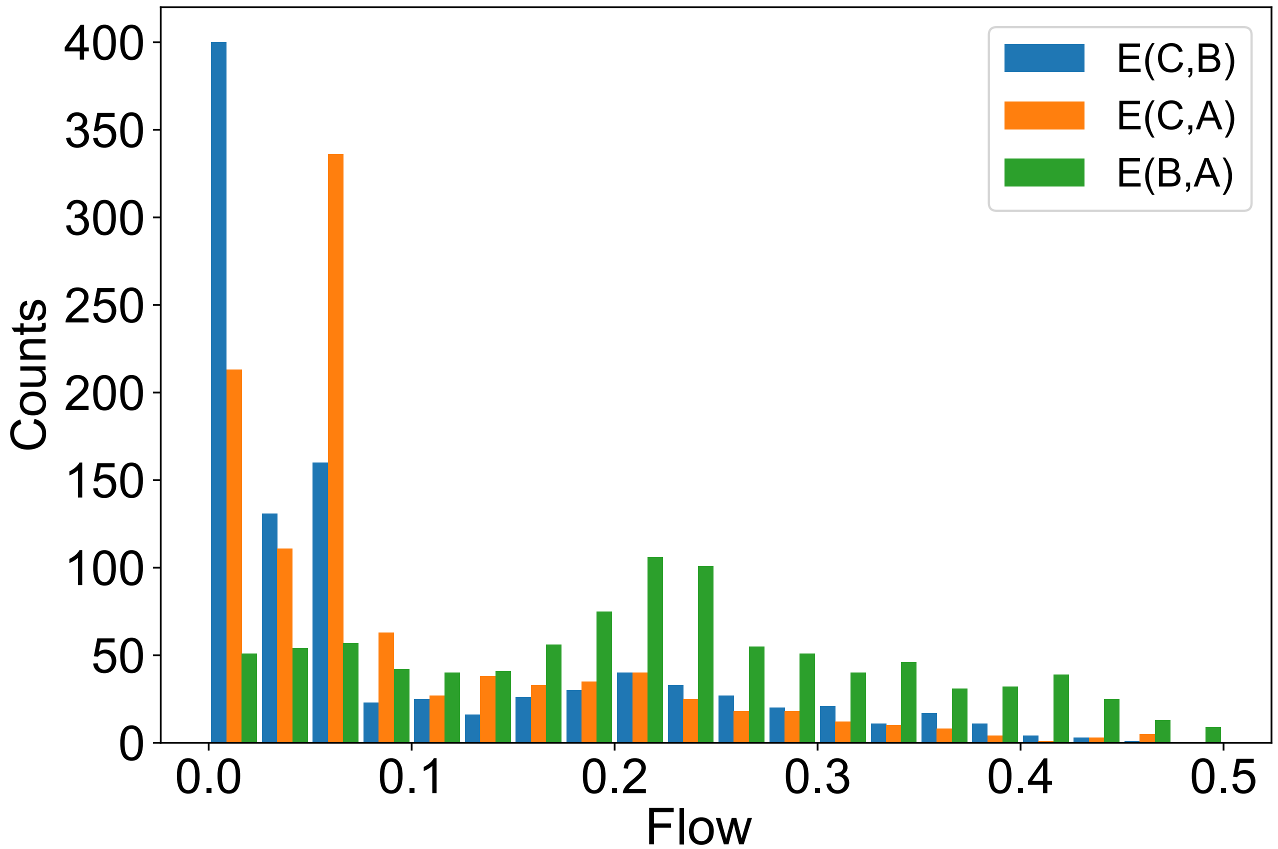


total: 72
C → B → A
E(C,B)
E(C,A)
E(B,A)
Flow

The B to A Class

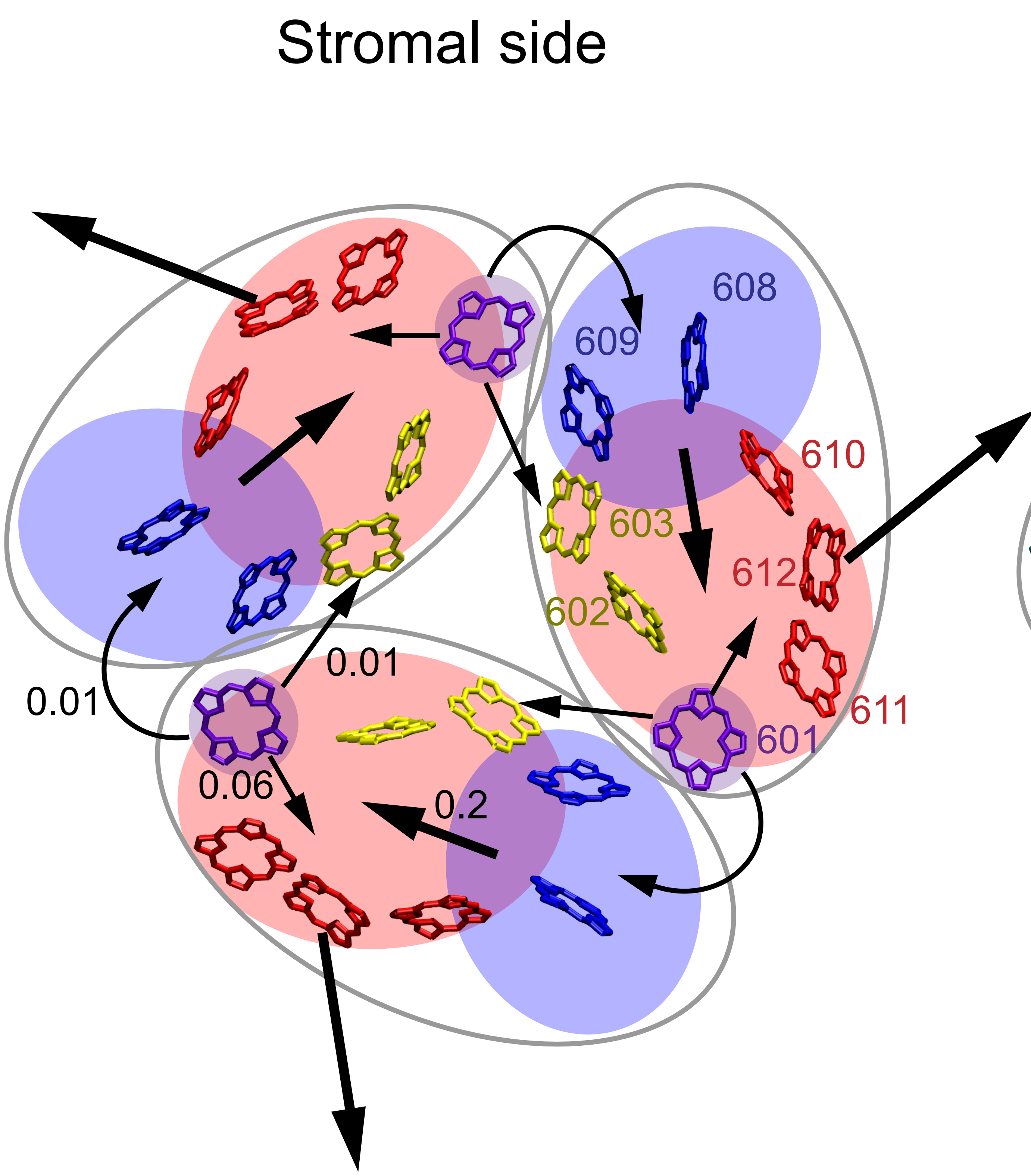


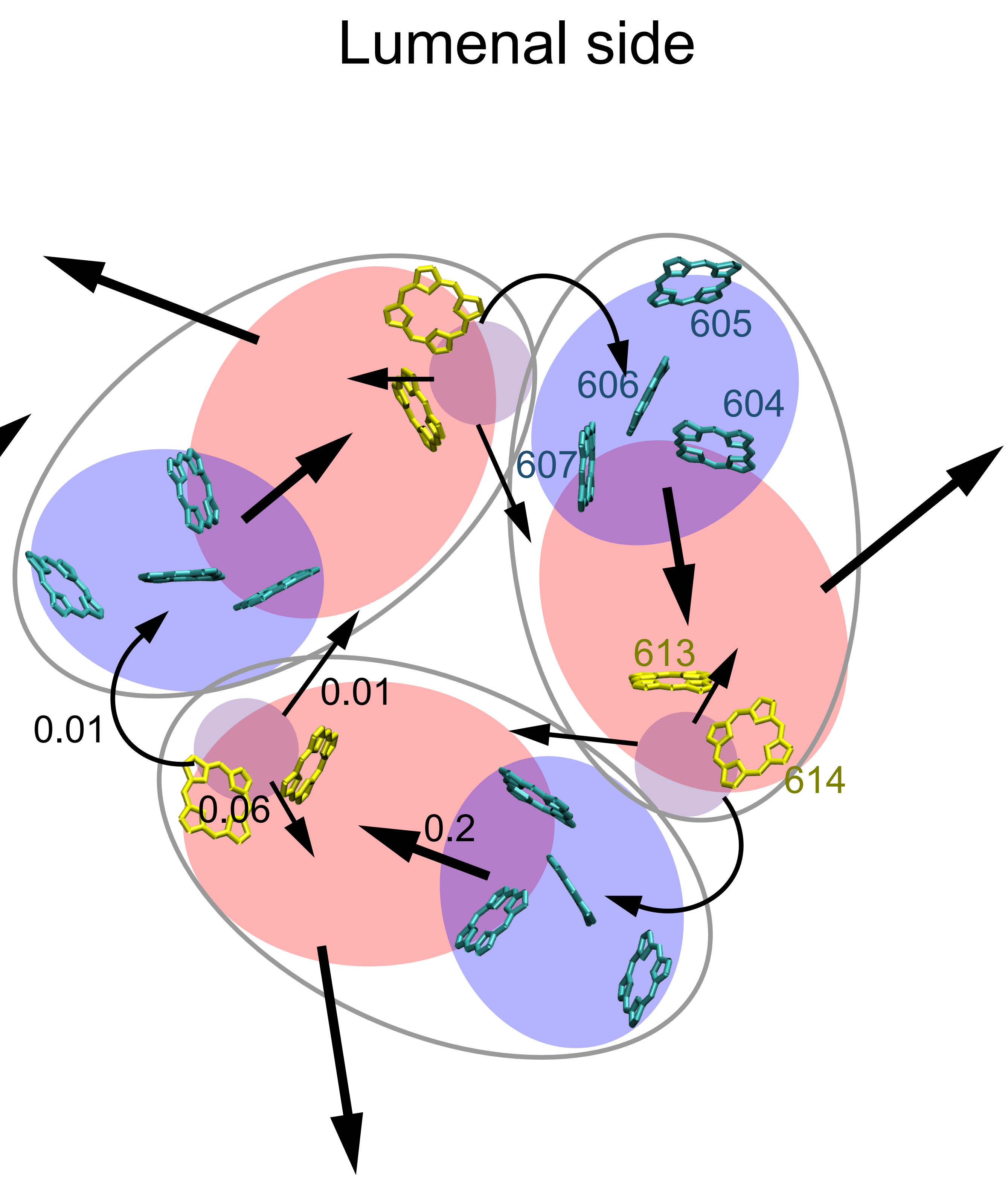




exciton	C_A	C_B	C_C	r_A	r_B	r_C
1	617	85	10	18%	3%	1%
2	612	99	1	17%	2%	0%
3	425	263	24	10%	6%	1%
4	389	283	40	8%	5%	1%
5	610	92	10	17%	3%	1%
6	325	338	49	6%	6%	1%
7	380	289	43	7%	5%	1%
8	28	579	105	1%	15%	3%
9	44	560	108	1%	14%	3%
10	28	573	111	0%	14%	3%
11	317	331	64	5%	5%	1%
12	330	321	61	6%	5%	1%
13	23	577	112	0%	14%	3%
14	49	61	602	3%	3%	81%

EET Model of LHCII





Conclusions

- Trimer form of LHCII is robust against disorders, and this could be one of the key reasons for LHCII to aggregate into trimer.
- The systematic minimum-cut coarse-graining approach provides an effective tool to elucidate the dynamics of energy transfer in photosynthetic light harvesting networks.