Supporting Information
Deep Learning for Optoelectronic Properties of Organic Semiconductors

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Supporting Information has 9 pages, 3 figures, and 2 tables.

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I. IMPLEMENTATION DETAILS OF DEEP NEURAL NETWORKS

In this section, we will provide additional implementation details of the deep neural networks (DNNs) used in the main text. As mentioned in the main text, we use the same hyperparameters as the original papers, unless otherwise stated. Particularly for SchNet, a cutoff of 5Å is used for the predictions of all electronic properties except the transition dipole moments, for which we use a cutoff of 25 Å. The dimension of embedding in SchNet is set to be 128, and we use three interaction blocks.

We train all DNN models with Adam optimizer[1] using a learning rate of 0.0001 and a batch size of 64. For SchNet, the decay rate is set to 1 (i.e., no decay) since we found that adding decay does not lead to noticeable improvement. We train all the models for a maximum of 750 epochs and use the validation set for early-stopping. The DNNs are implemented using Pytorch [2] and Deep Graph Library [3]. The codes of our implementations of MGCN, SchNet and MPNN can be found on Github [4], and we use DeepChem for DTNN [5].

II. BENCHMARK OF DFT FOR OLIGOTHIOPHENES

For organic semiconductors, range-separated hybrid density functionals are often required to reduce the self-interaction error, and Salzner and co-workers have conducted comprehensive benchmark studies on OTs [6, 7]. They found that ωB97XD and CAM-B3LYP show the best overall performance of all range-separated functionals they tested [6]. To further benchmark our DFT method, we computed the lowest singlet excited-state energies of isolated OTs against the reported results from a correlated wavefunction method (CC2 method) in Ref. 8. To make a fair comparison with the CC2 results, we optimized the geometries of OTs with planar constraints using B3LYP/cc-pVTZ following Ref. 8. TDDFT calculations were then performed with the Tamm-Dancoff approximation (TDA) at the level of CAM-B3LYP/6-31+G(d) to obtain the lowest singlet excited state energies. All the calculations were performed using PySCF. Density fitting was used for the TDDFT calculations with the heavy-aug-cc-pvdz-jkfit auxiliary basis set [9], as implemented in PySCF. As shown in Table S1, the predictions from CAM-B3LYP/6-31+G(d) are within 0.1 eV of those from CC2, whose error with respect to experimental estimate is shown to be around 0.15 eV in
average for the lowest lying excited-state energies of medium to large molecules [10]. Based on previous studies[6, 7, 10] and the benchmark results here, we estimate the average error of our TDDFT calculation in predicting the lowest lying excited-state energies of OTs to be around 0.2-0.3eV, within the range of the typical error of TDDFT (0.1-0.5eV) [11].

<table>
<thead>
<tr>
<th>Method</th>
<th>2T</th>
<th>3T</th>
<th>4T</th>
<th>5T</th>
<th>6T</th>
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<tr>
<td>CC2[8]</td>
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<td>3.57</td>
<td>3.21</td>
<td>2.96</td>
<td>-</td>
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<tr>
<td>CAM-B3LYP</td>
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<td>3.63</td>
<td>3.24</td>
<td>3.00</td>
<td>2.84</td>
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</table>

TABLE S1: Calculated excitation energies in eV for the lowest singlet excited state of isolated OTs. The results from the second-order approximate coupled cluster singles and doubles (CC2) are taken from Ref. 8. The geometries of OTs are optimized at the level of B3LYP/cc-pVTZ with the constraint of planarity following Ref. 8. TDDFT calculations with the CAM-B3LYP functional are performed with the basis set 6-31+G(d) using PySCF [12, 13].

III. MORE DISCUSSIONS ON ABSORPTION SPECTRAL SIMULATIONS

For the computation of the UV-Vis absorption spectrum of OT in dichloromethane, a single OT molecule was immersed in a simulation box of about 530 dichloromethane molecules, and classical MD simulation was performed in the NPT ensemble at 300 K and 1 atm using Desmond [14]. Martyna-Tobias-Klein scheme [15] was employed to maintain temperature and pressure with a coupling constant of 2.0 ps for both. The other simulation details are the same as those for isolated OTs described in Section 2 of the main text. Configurations of OTs were saved every 10 fs over a 10-ns trajectory for each OT, and then were fed into the SchNet models to compute the energies and transition dipole moments for the two lowest lying singlet states. Note that our SchNet models are trained against TDDFT results of isolated OTs. By using these SchNet models for OTs in solutions, we have neglected the effects of solvent on the excited-state properties of OTs, a reasonable approximation based on previous studies on OTs [16–22]. Table S2 shows the absorption maxima of the experimental absorption spectra of OTs in organic solvents of varying polarity, and it is clear that the solvatochromism of OTs is fairly small. It has been also shown theoretically that the solvent effects on OTs are small [21, 22].

In the experimental spectra of OTs in dichloromethane, there are extra peaks or shoulders on the blue side of the main peaks, and we attribute them to higher excited states. To verify this, we computed the first five excited-state energies and associated transition dipoles for
80,000 2T configurations harvested from the MD simulation of isolated 2T at 1000 K, and trained SchNet models for these properties. Following the same procedure described in the main text, we re-computed the absorption spectrum of 2T in dichloromethane including the first five excited states, and as shown in Fig. S1, a second peak shows up at around 5.8 eV, leading to an improved agreement between calculated and experimental spectra. Our calculation still underestimates the intensity of the high-energy peak, and possibly overestimates the peak position. More excited states may be still needed, but more importantly the errors associated with higher excited states may be even larger than that of the lowest-lying excited state. For 6T, our test calculation suggests that at least 30 excited states are needed to cover the spectral range up to 5.0eV.

<table>
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<tr>
<th>Solvent</th>
<th>2T</th>
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<th>5T</th>
<th>6T</th>
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<td>3.17</td>
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</table>

TABLE S2: Absorption maxima of the experimental absorption spectra of OTs in different solvents in the unit of eV.

In the main text, the SchNet models for excited-state energies and associated transition dipoles are trained on 80,000 configurations for each OT. We repeated the training process but with only 5,000 randomly chosen configurations, and the resulting absorption spectra are displayed in Fig. S2. The agreement between calculated and experimental spectra is almost as good as that based on 80,000 training configurations (see Fig. 6 in the main text) except two minor differences: the spectra are slightly red-shifted; and the spectra of 5T and 6T are slightly narrower. This is consistent with the dependence of MAEs on training data size shown in Fig. 2 of the main text, demonstrating the effectiveness of SchNet in predicting excited-state properties of OSCs even with relatively small datasets.
FIG. S1: Calculated (blue solid line) and experimental[16] (black solid line) absorption spectra of 2T in dichloromethane. The contributions from the first five excited states to the calculated spectra are shown as colored dashed lines. All the calculated spectra are uniformly red-shifted by 0.3eV, and both the calculated and experimental spectra are scaled to have the same peak height.
FIG. S2: Calculated (blue solid lines) and experimental[16] (black solid lines) absorption spectra of OTs in dichloromethane. The contributions from the first two excited states to the calculated spectra are shown as green and red dashed lines, respectively. All the calculated spectra are generated from SchNet models trained on 5000 configurations, and are uniformly red-shifted by 0.3eV. Both the calculated and experimental spectra are scaled to have the same peak height.
IV. COMPARISONS OF RESULTS FROM SCHNET AND TDDFT

In Fig. S3 we compare the first excited-state energies of 6T obtained from SchNet and TDDFT. Fig S3a shows that SchNet is capable of accurately capturing the dynamics of the excited-state energy, which are critical to the modeling of exciton dynamics in OSCs.[23, 24] Fig. S3b furthers demonstrate the capability of SchNet since no outlier or systematic error is observed.

FIG. S3: (a) Excited state energies of gas-phased 6T from SchNet (dashed line) and TDDFT (solid line) as a function of time. The trajectory is obtained MD simulations at 1000K. (b) Comparison of 1000 6T excited state energies obtained from SchNet and TDDFT.


