

# Electronic Supplementary Information (ESI) for “Absorption and fluorescence properties of oligothiophene biomarkers from long-range-corrected time-dependent density functional theory”

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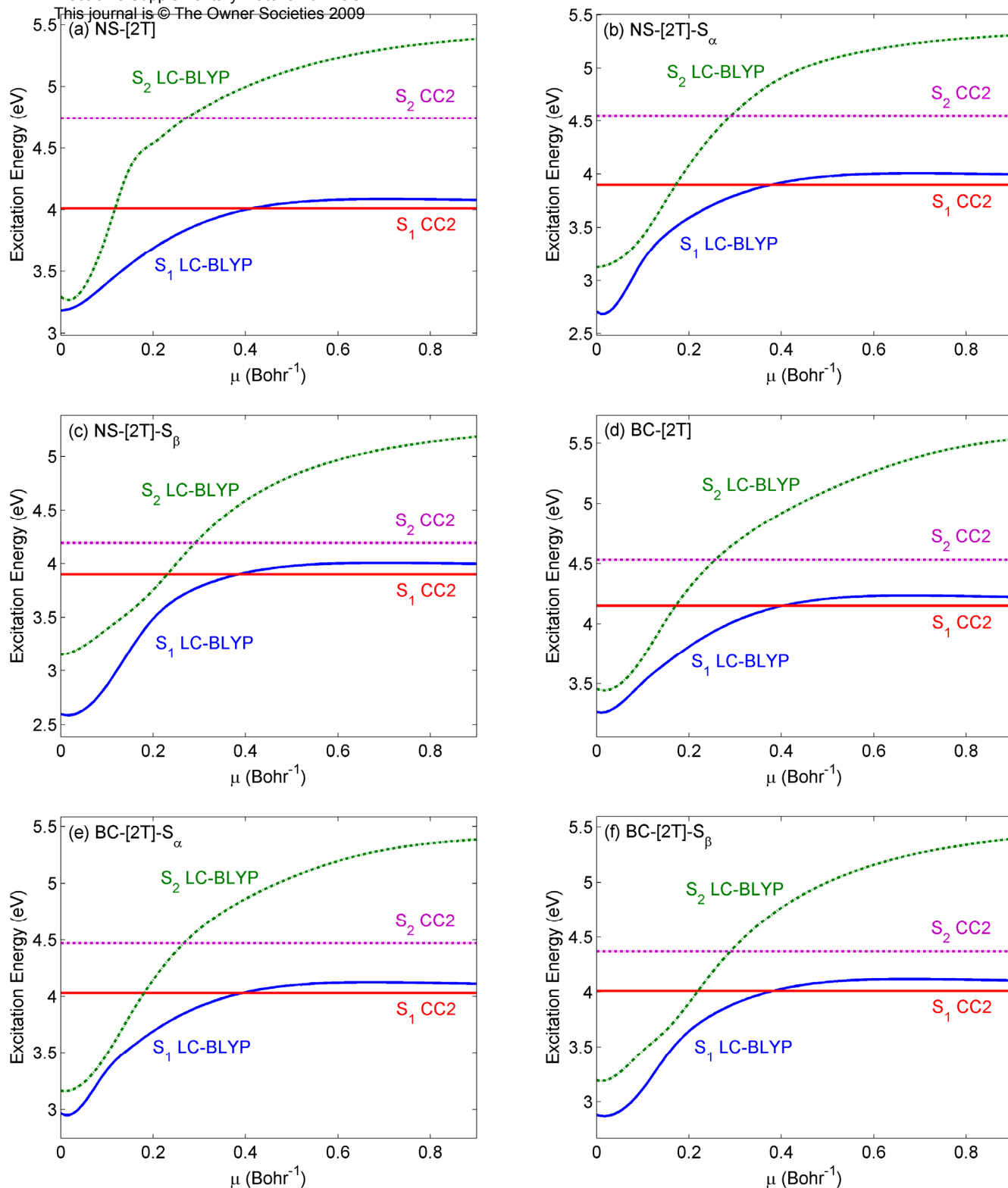
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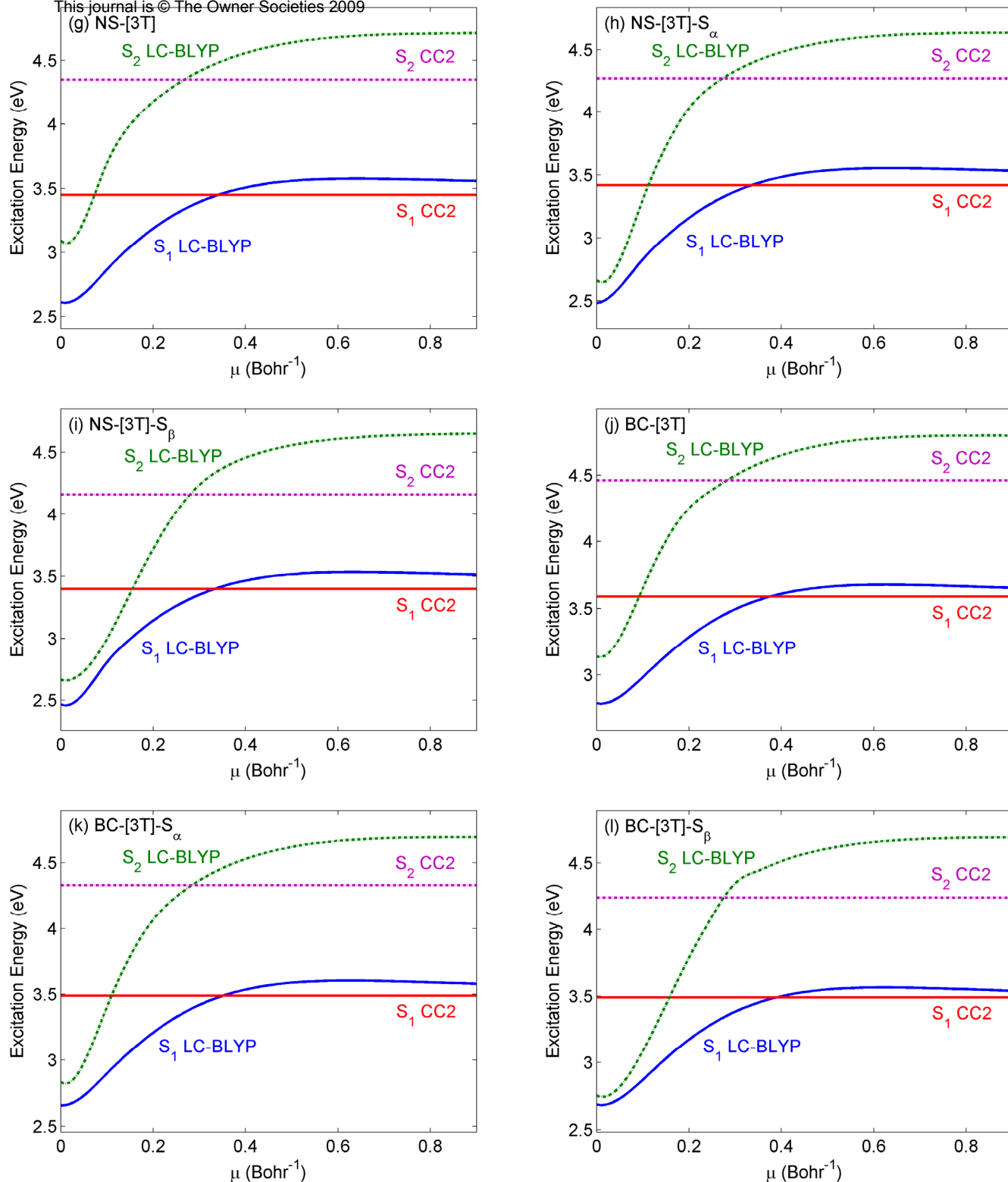
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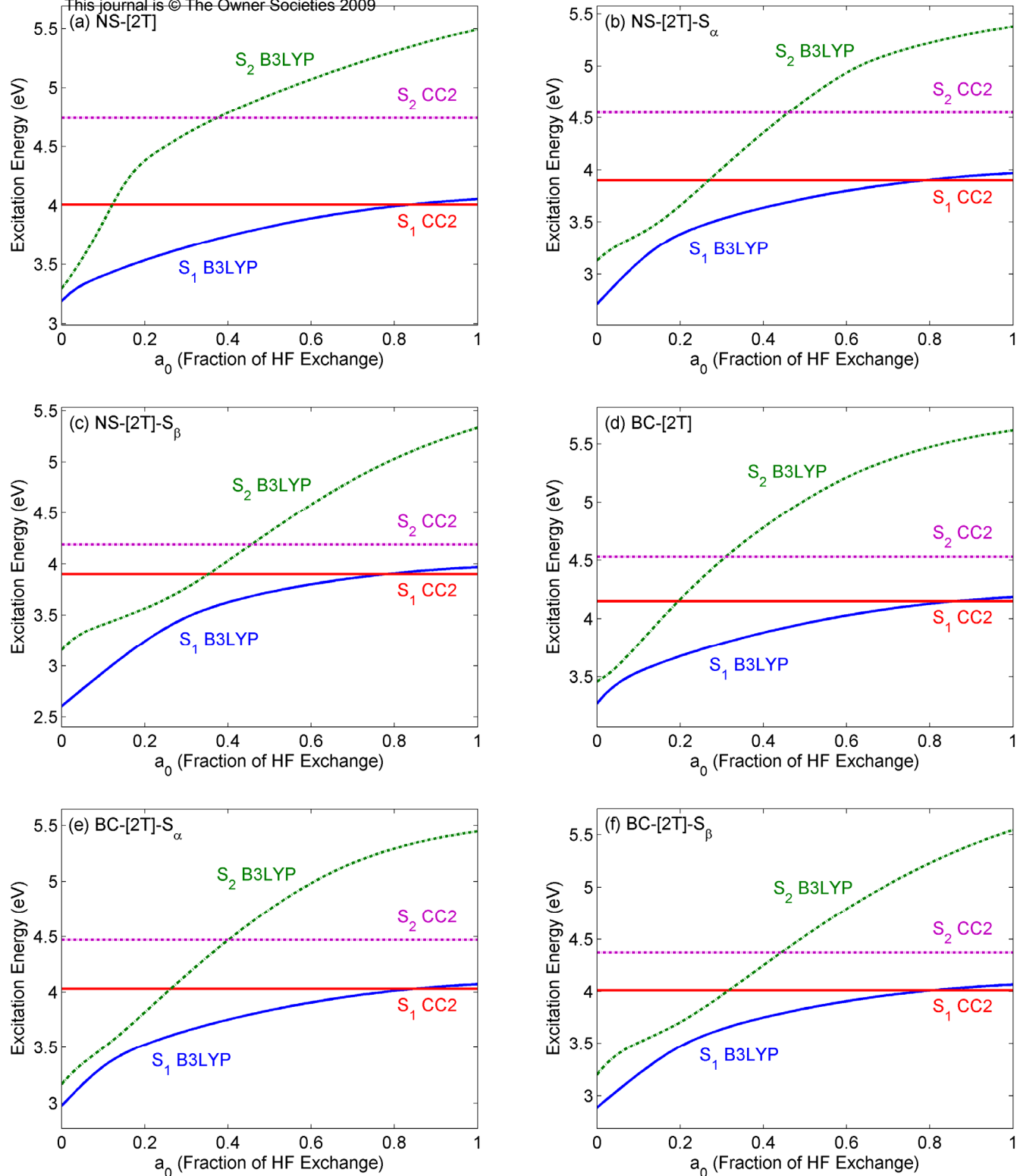
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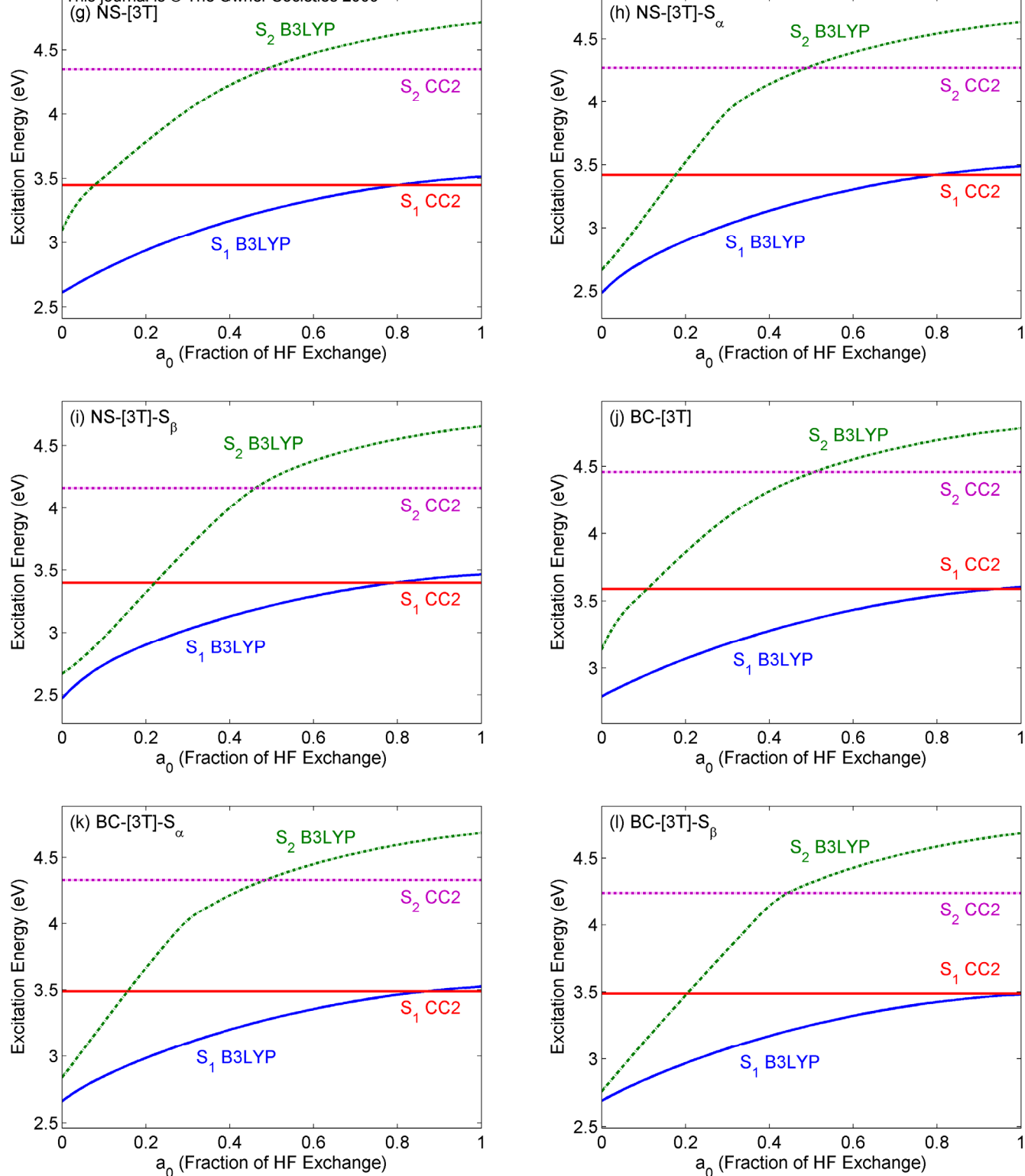
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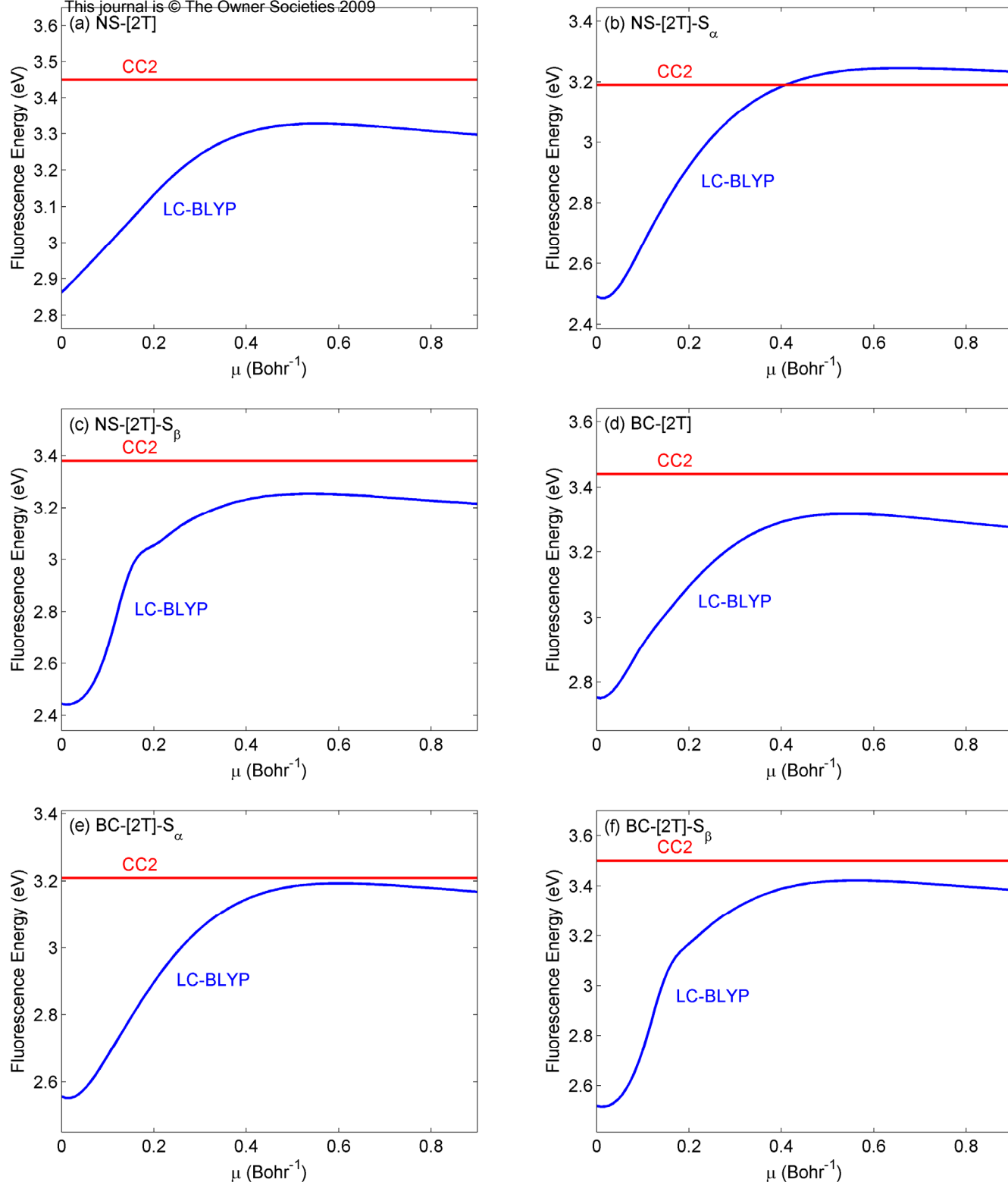
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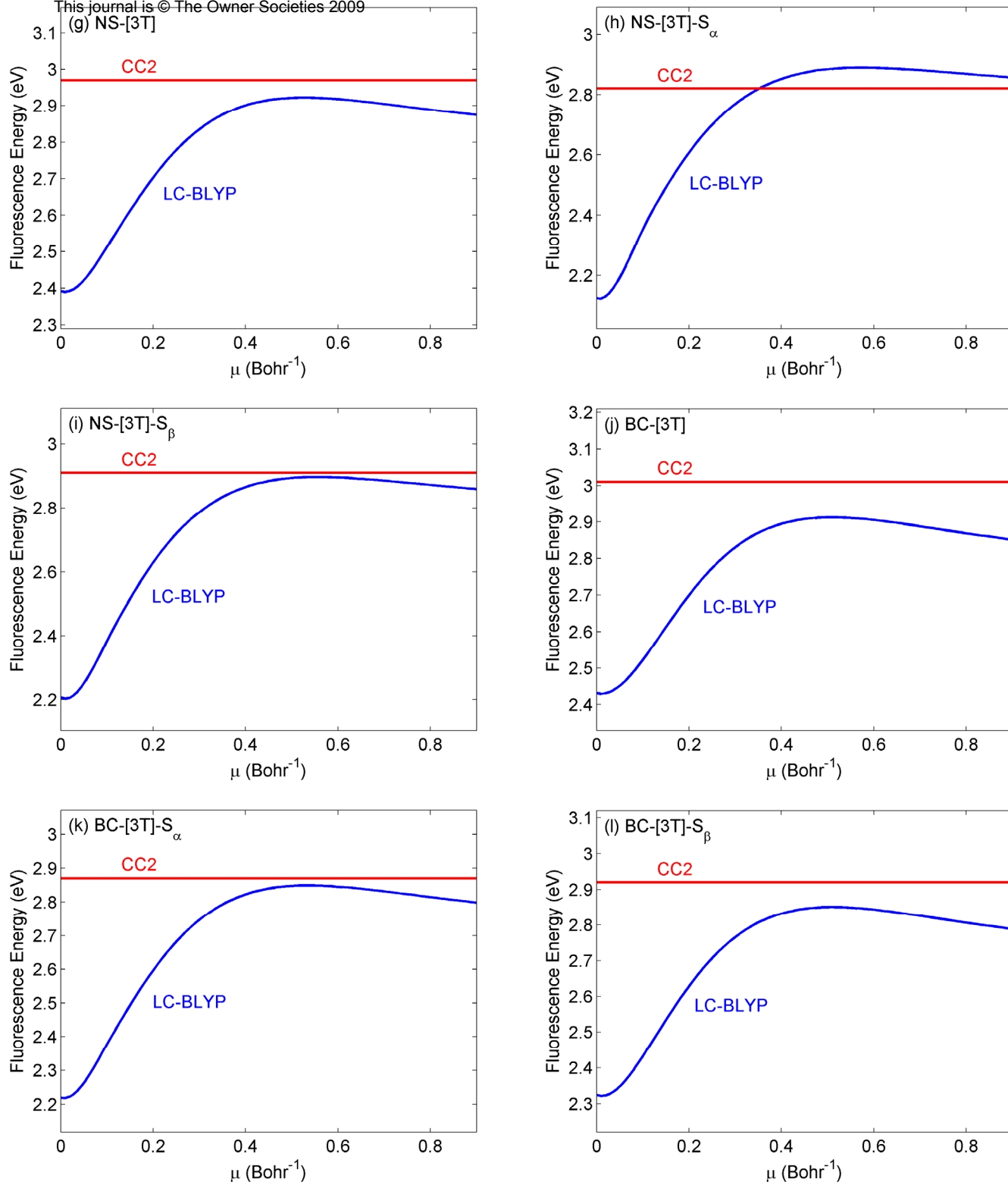
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**Fig. ESI-2 (g) – (l)**  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  vertical excitation energies as a function of the HF exchange fraction  $a_0$  in a B3LYP-like functional. The horizontal lines represent the CC2/ATZVP excitation energies, and the curved lines denote the TDDFT B3LYP/ATZVP calculations. The solid lines denote  $S_1 \leftarrow S_0$  excitation energies while dashed lines represent  $S_2 \leftarrow S_0$  excitations.

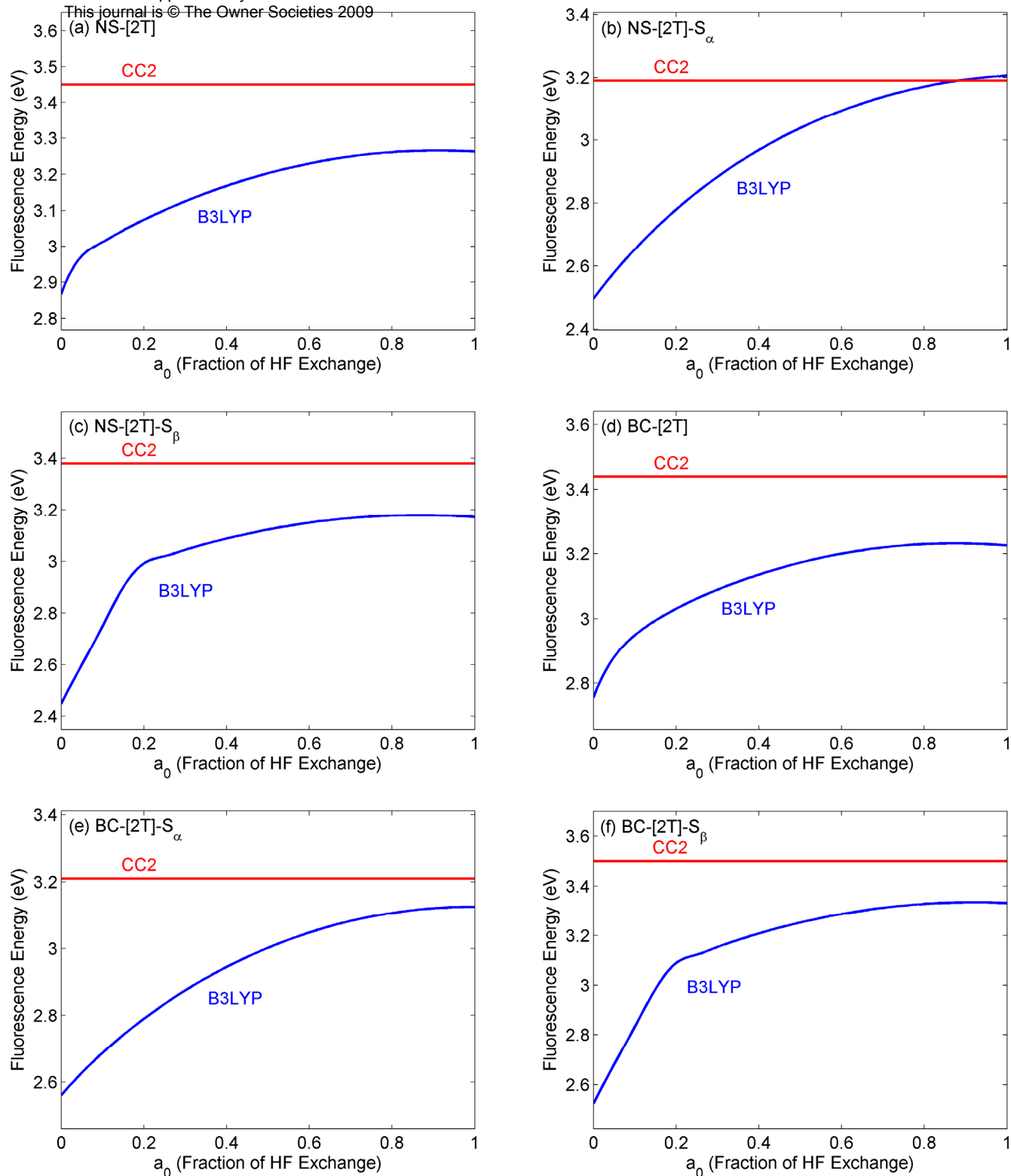


**Fig. ESI-3 (a) – (f)**  $S_1 \rightarrow S_0$  fluorescence energies as a function of the LC-BLYP range parameter  $\mu$ . The horizontal line represents the CC2/ATZVP excitation energy, and the curved line denotes the TDDFT LC-BLYP/ATZVP calculations.

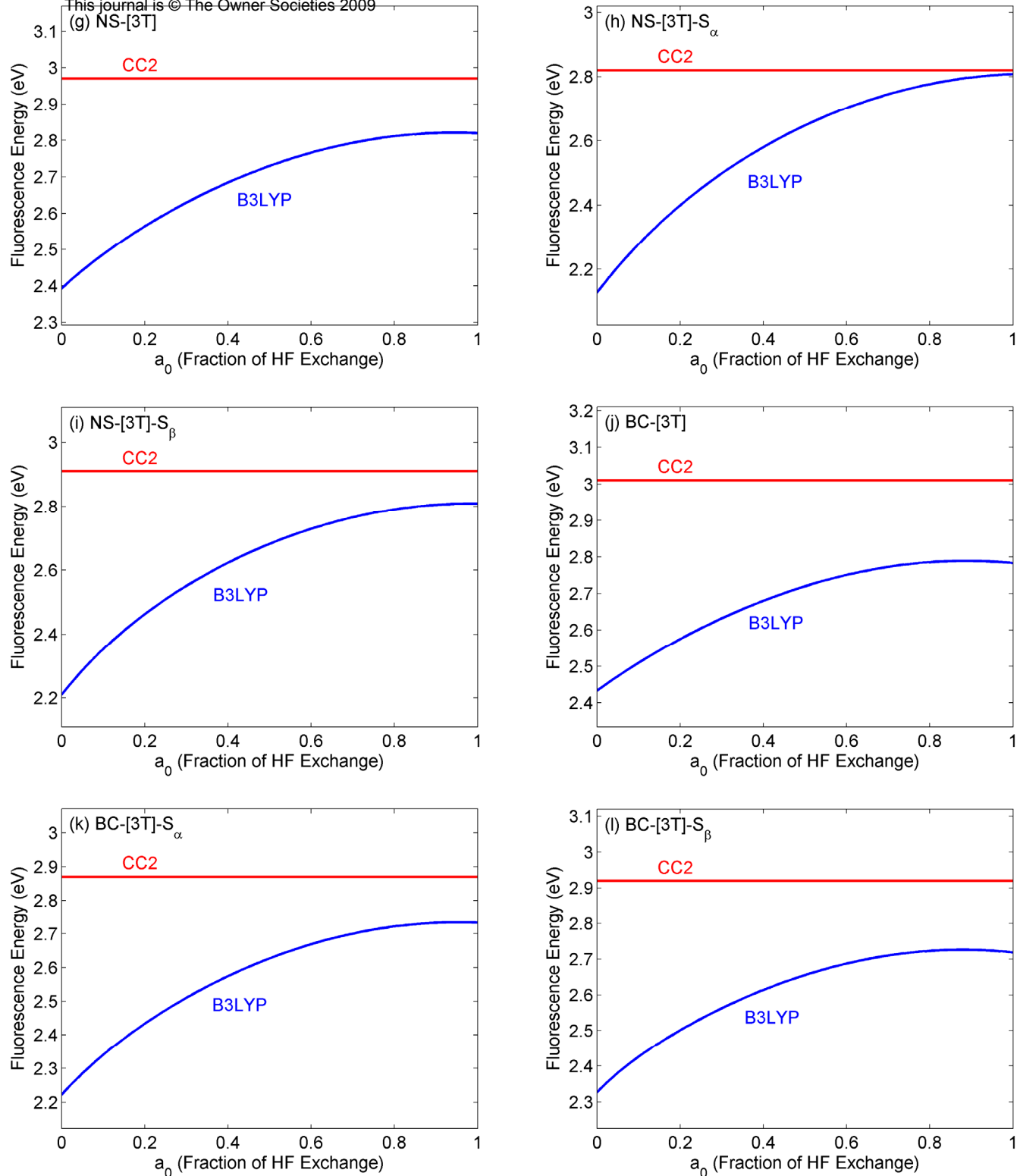


**Fig. ESI-3 (g) – (l) (continued)**  $S_1 \rightarrow S_0$  fluorescence energies as a function of the LC-BLYP range parameter  $\mu$ . The horizontal line represents the CC2/ATZVP excitation energy, and the curved line denotes the TDDFT LC-BLYP/ATZVP calculations.





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**Fig. ESI-4 (g) – (l)**  $S_1 \rightarrow S_0$  fluorescence energies as a function of the HF exchange fraction  $a_0$  in a B3LYP-like functional. The horizontal line represents the CC2/ATZVP excitation energy, and the curved line denotes the TDDFT B3LYP/ATZVP calculations.

**Table ESI-1** BHHLYP and LC-BLYP  $\mu=0.47$   $S_1/S_2 \leftarrow S_0$  excitation energies and oscillator strengths for the bithiophene systems. All properties were computed with the ATZVP basis on B3LYP/TZVP-optimized geometries.

| System              | State | BHHLYP                |               | LC-BLYP ( $\mu = 0.47$ ) |               |
|---------------------|-------|-----------------------|---------------|--------------------------|---------------|
|                     |       | $E_{\text{abs}}$ (eV) | Osc. strength | $E_{\text{abs}}$ (eV)    | Osc. strength |
| NS-[2T]             | $S_1$ | <b>3.82</b>           | 0.64          | <b>4.05</b>              | 0.63          |
|                     | $S_2$ | <b>4.93</b>           | 0.02          | <b>5.10</b>              | 0.03          |
| NS-[2T]- $S_\alpha$ | $S_1$ | <b>3.73</b>           | 0.79          | <b>3.97</b>              | 0.77          |
|                     | $S_2$ | <b>4.66</b>           | 0.01          | <b>5.04</b>              | 0.01          |
| NS-[2T]- $S_\beta$  | $S_1$ | <b>3.72</b>           | 0.53          | <b>3.96</b>              | 0.55          |
|                     | $S_2$ | <b>4.30</b>           | 0.06          | <b>4.76</b>              | 0.03          |
| BC-[2T]             | $S_1$ | <b>3.96</b>           | 0.53          | <b>4.20</b>              | 0.51          |
|                     | $S_2$ | <b>5.01</b>           | 0.01          | <b>5.06</b>              | 0.01          |
| BC-[2T]- $S_\alpha$ | $S_1$ | <b>3.83</b>           | 0.67          | <b>4.08</b>              | 0.65          |
|                     | $S_2$ | <b>4.74</b>           | 0.00          | <b>5.00</b>              | 0.01          |
| BC-[2T]- $S_\beta$  | $S_1$ | <b>3.83</b>           | 0.45          | <b>4.08</b>              | 0.45          |
|                     | $S_2$ | <b>4.52</b>           | 0.02          | <b>4.94</b>              | 0.02          |

**Table ESI-2** BHHLYP and LC-BLYP  $\mu=0.47$  S<sub>1</sub>/S<sub>2</sub> ← S<sub>0</sub> excitation energies and oscillator strengths for the terthiophene systems. All properties were computed with the ATZVP basis on B3LYP/TZVP-optimized geometries.

| System                                   | State          | BHHLYP                |               | LC-BLYP ( $\mu = 0.47$ ) |               |
|------------------------------------------|----------------|-----------------------|---------------|--------------------------|---------------|
|                                          |                | $E_{\text{abs}}$ (eV) | Osc. strength | $E_{\text{abs}}$ (eV)    | Osc. strength |
| NS-[3T]                                  | S <sub>1</sub> | <b>3.26</b>           | 1.02          | <b>3.55</b>              | 1.00          |
|                                          | S <sub>2</sub> | <b>4.36</b>           | 0.00          | <b>4.62</b>              | 0.00          |
| NS-[3T]-S <sub><math>\alpha</math></sub> | S <sub>1</sub> | <b>3.23</b>           | 1.17          | <b>3.53</b>              | 1.14          |
|                                          | S <sub>2</sub> | <b>4.28</b>           | 0.01          | <b>4.54</b>              | 0.01          |
| NS-[3T]-S <sub><math>\beta</math></sub>  | S <sub>1</sub> | <b>3.22</b>           | 0.98          | <b>3.51</b>              | 0.96          |
|                                          | S <sub>2</sub> | <b>4.23</b>           | 0.02          | <b>4.53</b>              | 0.02          |
| BC-[3T]                                  | S <sub>1</sub> | <b>3.36</b>           | 0.94          | <b>3.65</b>              | 0.90          |
|                                          | S <sub>2</sub> | <b>4.45</b>           | 0.00          | <b>4.71</b>              | 0.00          |
| BC-[3T]-S <sub><math>\alpha</math></sub> | S <sub>1</sub> | <b>3.28</b>           | 1.07          | <b>3.58</b>              | 1.03          |
|                                          | S <sub>2</sub> | <b>4.34</b>           | 0.01          | <b>4.60</b>              | 0.01          |
| BC-[3T]-S <sub><math>\beta</math></sub>  | S <sub>1</sub> | <b>3.25</b>           | 0.85          | <b>3.54</b>              | 0.82          |
|                                          | S <sub>2</sub> | <b>4.31</b>           | 0.01          | <b>4.58</b>              | 0.01          |

**Table ESI-9** BHHLYP and LC-BLYP  $\mu=0.47$   $S_1 \rightarrow S_0$  fluorescence energies and oscillator strengths for all 12 oligothiophene biomarkers. All properties were computed with the ATZVP basis on TDDFT B3LYP/TZVP-optimized geometries of the  $S_1$  state.

| System              | BHHLYP        |               | LC-BLYP ( $\mu = 0.47$ ) |               |
|---------------------|---------------|---------------|--------------------------|---------------|
|                     | $E_{fl}$ (eV) | Osc. strength | $E_{fl}$ (eV)            | Osc. strength |
| NS-[2T]             | <b>3.20</b>   | 0.64          | <b>3.32</b>              | 0.62          |
| NS-[2T]- $S_\alpha$ | <b>3.04</b>   | 0.76          | <b>3.22</b>              | 0.74          |
| NS-[2T]- $S_\beta$  | <b>3.12</b>   | 0.57          | <b>3.25</b>              | 0.56          |
| BC-[2T]             | <b>3.17</b>   | 0.53          | <b>3.31</b>              | 0.51          |
| BC-[2T]- $S_\alpha$ | <b>3.00</b>   | 0.67          | <b>3.18</b>              | 0.65          |
| BC-[2T]- $S_\beta$  | <b>3.25</b>   | 0.50          | <b>3.41</b>              | 0.49          |
| NS-[3T]             | <b>2.73</b>   | 1.05          | <b>2.92</b>              | 1.00          |
| NS-[3T]- $S_\alpha$ | <b>2.65</b>   | 1.21          | <b>2.88</b>              | 1.16          |
| NS-[3T]- $S_\beta$  | <b>2.68</b>   | 0.99          | <b>2.89</b>              | 0.97          |
| BC-[3T]             | <b>2.72</b>   | 0.96          | <b>2.91</b>              | 0.91          |
| BC-[3T]- $S_\alpha$ | <b>2.63</b>   | 1.12          | <b>2.84</b>              | 1.06          |
| BC-[3T]- $S_\beta$  | <b>2.65</b>   | 0.88          | <b>2.85</b>              | 0.84          |