Measurement of energy levels of BAlq, BCP and DTBT using cyclic voltammetry (CV).

HOMO level of BAlq was measured directly from the oxidation potential using the ferrocene for the calibration and dichloromethane as the solvent (Figure S-1). The HOMO levels of BCP and DTBT, however, were not measurable directly from the oxidation potential of the materials because they were beyond the stability window of the solvent we used to measure the HOMO level. The solvent, dichloromethane, is known as the material possessing the highest stability in terms of the oxidation, to our knowledge, which is the 1.3 V against Ag/Ag+ reference potential when measured as the onset potential. This indicates that the HOMO levels of the materials are lower than - 6.0 eV (oxidation potential of ferrocene in the solvent is 0.08 eV measured as the onset potential).

Instead, we measured the LUMO level from the reduction potential of BCP and DTBT and the HOMO level was calculated using the optical bandgaps of the materials. The results are shown in the figure S-2 and S-3, respectively. N,N-dimethylformamide was used as the solvent, which has large stability in the reduction. The ferrocene reference is also included for the calibration. The measured LUMO levels are -2.56 and -3.01 eV for BCP and DTBT, respectively, after calibration using ferrocene. Since the optical bandgaps are 3.55 and 3.50 eV for BCP and DTBT, respectively, the calculated HOMO levels are -6.11 and -6.51 eV, respectively, .

Discrepancy of the HOMO energy level of BCP between the value obtained by the above method and references is apparent. The HOMO levels reported in references are spread between -6.4 to -6.7 eV (-6.4 eV in the references S.1-S.3, -6.5 eV in the references of S.4-S.8, and -6.7 eV in S.9-S.12) and more recent references use the value

of -6.4 or -6.5 eV. Still there is discrepancy in the values. One needs to note that the HOMO level of BCP was measured by UV photoelectron spectroscopy (UPS) in the references.

Measurement of HOMO levels by CV and UPS was well compared in the reference S.13. The authors extracted the relationship between them as follows.

$$E_{HOMO}\,(\mathrm{UPS}) = -(1.4 \pm 0.1)\cdot(qV_{CV}) - (4.6 \pm 0.08)\ \mathrm{eV}, \qquad (S.1)$$

The HOMO level of -6.11 eV of BCP measured by CV technique corresponds to -6.42±0.1 eV in UPS measurement, which is well consistent with the reference values of -6.4~-6.5 eV. This result confirms the accuracy of the experiment in the measurement of HOMO levels by the CV technique. The HOMO level of DTBT becomes -6.99 eV, which is a very large negative value.

In the revised manuscript, we used the value obtained by the CV measurement for the consistency of the energy levels of BAlq. The qualitative description of hole blocking ability of DTBT compared to BCP and BAlq is still correct because it is related to the relative position of HOMO levels, not by the absolute values.

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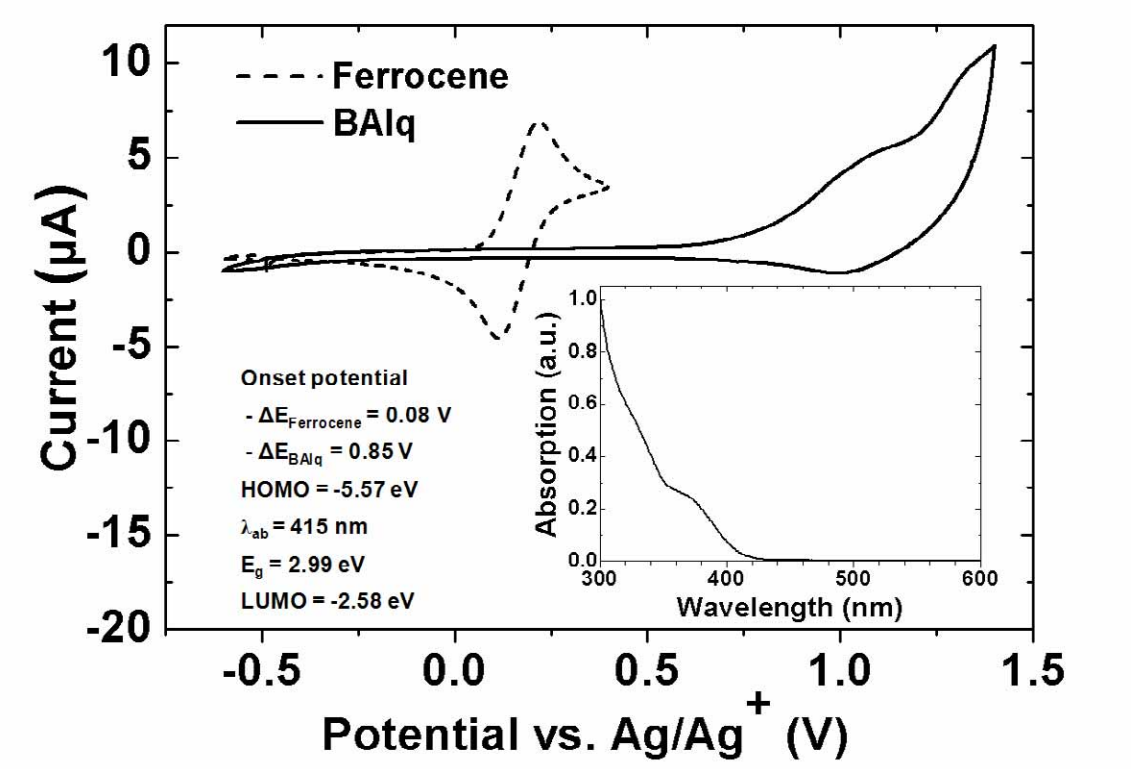


Figure S.1 Cyclovoltammety (CV) diagram of BAlq in dichloromethane. CV of ferrocene is shown for the calibration. Inset shows the absorption spectrum of BAlq.

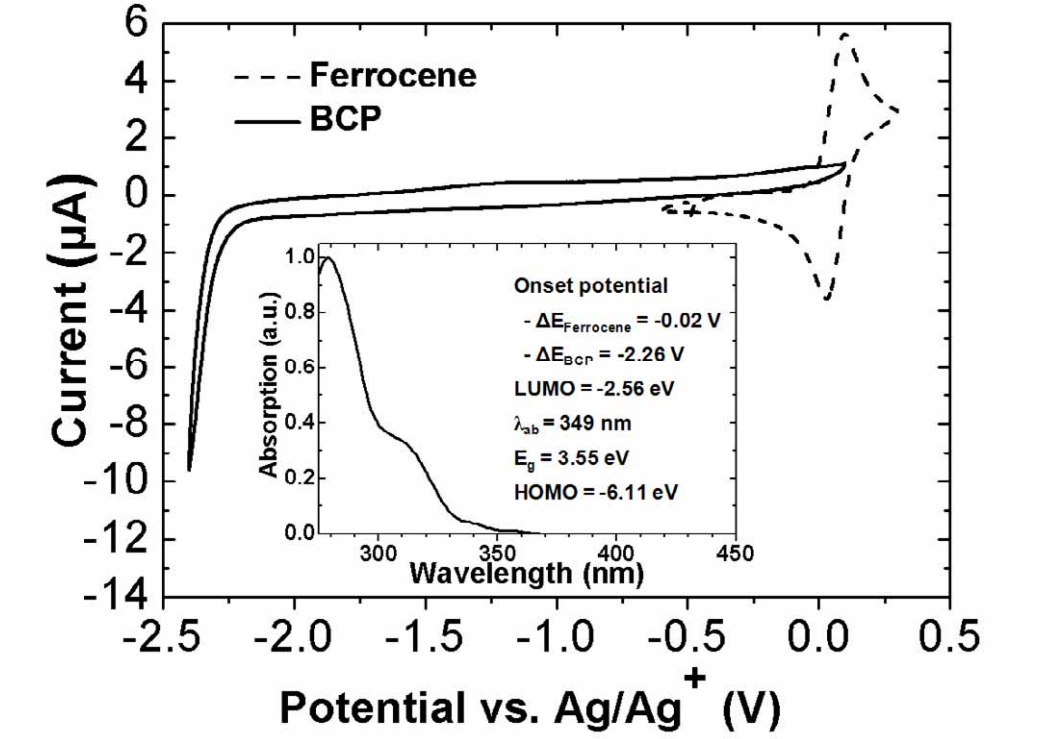


Figure S.2. Cyclovoltammety (CV) diagram of BCP in N,N-dimethylformamide. CV of ferrocene is shown as a reference. Inset shows the absorption spectrum of BCP.

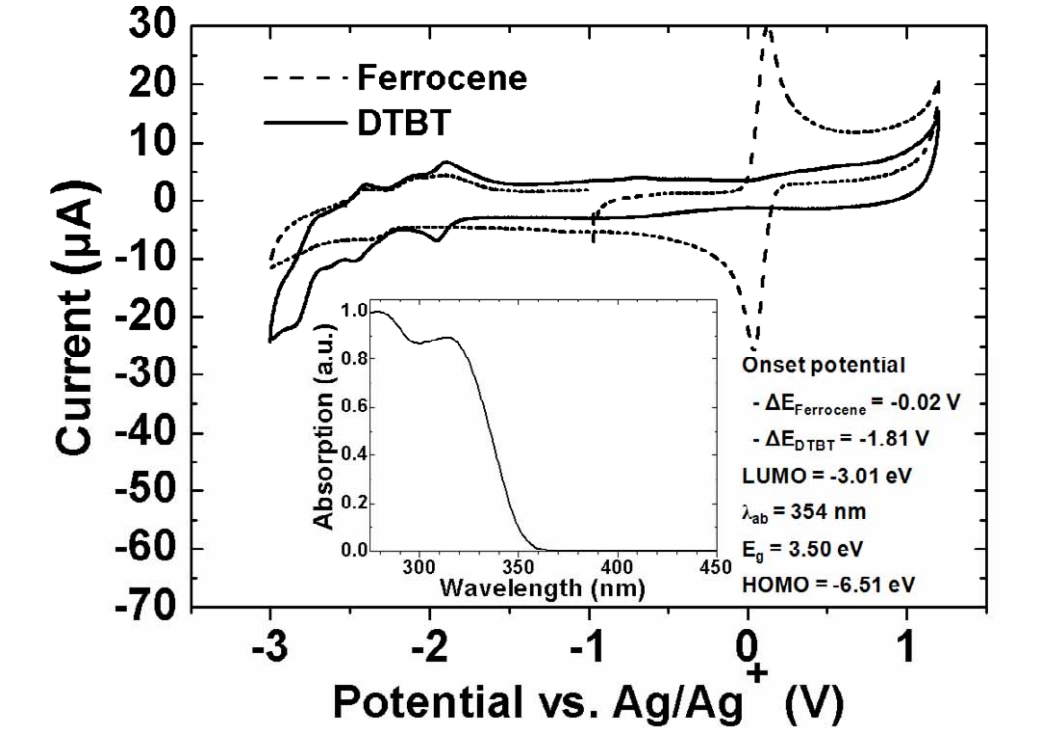


Figure S.3. Cyclovoltammety (CV) diagram of DTBT in N,N-dimethylformamide. CV of ferrocene is shown as a reference. Inset shows the absorption spectrum of DTBT.