Figure S1. (a) Binding curves for the neutral quaterthiophene (4T) and radical quencher species. Geometries of the (b) 4T-GxMe pair, (c) 4T-PTIO pair, and (d) 4T-TEMPO pair at the equilibrium distances seen looking down on the x-z plane. (e) Orientations of the individual species seen looking down the x-y plane (red: x, green: y, blue: z). The species were aligned in a co-facial orientation in the following manner. For 4T, the 2- and 5- carbons of the thiophene ring nearest the geometric center of the molecule were aligned along the x-axis, and the plane of this thiophene ring was aligned with the x-y plane by orienting the cross product of the x-axis and the C-S bond with the positive z-axis. For GxMe, the C2 axis was aligned with the y-axis, and the two carbons closest to the C2 axis were aligned with the x-axis. For PTIO, the C2 axis was aligned with the x-axis, and the phenyl ring was aligned with the x-y plane by orienting the 3- and 5- carbons of the phenyl ring with the y-axis. For TEMPO, the mirror plane, or the vector between the nitrogen and the 4-carbon, was aligned with the x-axis, and the 2- and 6-carbons were aligned with the y-axis. The TEMPO molecule was oriented so the less sterically-hindered face was facing the negative z-direction. All molecules were translated such that their centroids were aligned with the origin. To generate the 4T-radical pairs, the two molecules were superimposed with their centroids overlapping, and the radical species was displaced a given distance along the positive z-axis.
Figure S2. Absorbance spectra of P3HT in solution (60 μM of repeat units in chloroform) blended with varying concentrations of (a) PCBM, (b) the galvinoxyl radical, (c) the PTIO radical, and (d) the TEMPO radical. The absorbance spectra of solutions with 0.1 mM of small molecule and no P3HT are indicated with a dashed line. The spectra are the sum of the spectra of the individual components, indicating that no supramolecular complexes are forming in the ground state when the materials are co-dissolved in solution.
Figure S3. Reduction of the intensity of fluorescence spectra of P3HT in solution (60μM of repeat units in chloroform) upon addition of up to 1 mM of (a) PCBM, (b) the galvinoxyl radical, (c) the PTIO radical, and (d) the TEMPO radical, showing that the galvinoxyl and PTIO radical species act as fluorescence quenchers with nearly the same quenching ability as PCBM, while the TEMPO radical does not show this effect. The excitation wavelength was 500 nm. All spectra were corrected for the inner filter effect.
**Figure S4.** Absorbance spectra of the neutral galvinoxyl and PTIO radicals and the reduced galvinylate and PTIO anions. The galvinoxyl species were measured at a 0.01 mM concentration in ethanol, and the PTIO species were measured at a 0.1 mM concentration in water. These concentrations were chosen so that the samples would have similar optical densities for comparison purposes. The galvinylate anion shows a strong absorbance near 560 nm, while the PTIO anion shows a broad absorbance near 325 nm.
Figure S5. AFM phase images of P3HT thin films with small molecule additives present at a loading of 10%, on a molar basis. Scale bars represent 50 nm.
Derivation of the Inner Filter Effect Correction Formula

**Figure S6.** Illustrations for the inner filter effect derivation. (a) Depiction of how the light going to and coming from an infinitesimal area element is attenuated and (b) the definition of the coordinates used in the derivation.

The inner filter effect is composed of two parts, the primary inner filter effect, which is the absorption of the excitation beam, and the secondary inner filter effect, which is the absorption of the fluorescence signal. In a typical fluorimeter, the fluorescence signal is measured at a right (i.e., 90°) angle to the excitation beam, so that the excitation beam does not saturate the photodetector. Thus, the primary and secondary inner filter effects arise from attenuation in perpendicular directions. In the absence of an inner filter effect, the number of photons generated is the product of the photon flux entering the sample, the width of the excitation beam, the fraction of light absorbed by the fluorophore in the sample, and the quantum yield of the fluorophore (number of photons emitted per photon absorbed). This can be expressed with Equation S1.

\[
I_{em} = I_{ex} W (1 - 10^{-\epsilon_{F,ex} L c_F}) \Phi_Q \quad (\text{Eq. S1})
\]

Here, \(I_{em}\) is the fluorescence intensity, \(I_{ex}\) is the emission intensity, \(\epsilon_{F,ex}\) is the Beer-Lambert constant of the fluorophore at the excitation wavelength, \(L\) and \(W\) are the length and width of the sample, \(c_F\) is the concentration of the fluorophore, and \(\Phi_Q\) is the quantum yield. If the inner filter effect is to be taken into account, then we can consider an infinitesimal area over
which the attenuation is negligible and integrate over the entire sample. Within the infinitesimal area, the number of photons generated is given by Equation S1, except with $L$ and $W$ replaced by $dx$ and $dy$ and with the excitation intensity and emission intensity attenuated by the transmittance of the respective wavelengths through the sample to that point (Figure S6a). The equation is as follows.

$$I_{obs}(x, y) = I_{ex}(1 - e^{-e_{ex}dx})dy \Phi Q 10^{-a_{ex}x}10^{-a_{em}y}$$  \hspace{1cm} (Eq. S2)

Here, $a_{ex}$ and $a_{em}$ are the absorbance per unit length at the excitation and emission wavelengths, equal to the sum of the products of the concentration of the absorbing species in the solution and the Beer-Lambert constant for that species at the excitation or emission wavelength.

$$a_{em/ex} = \sum e_{em/ex}c_i$$  \hspace{1cm} (Eq. S3)

In this work, the only absorbing species are the fluorophore and the quencher. Equation S3 can be integrated if the exponential term is replaced with its Taylor series expansion in $dx$ and all terms of second-order and higher are discarded, which is a valid assumption here as $dx$ is infinitesimally small. This gives the following expression.

$$I_{obs}(x, y) = \ln(10) I_{ex}e_{ex}c_F \Phi Q 10^{-a_{ex}x}10^{-a_{em}y}dx\,dy$$  \hspace{1cm} (Eq. S4)

In turn, Equation S4 can be integrated to yield the following.

$$I_{ob} = I_{ex}e_{ex}c_F \Phi Q \frac{(10^{-a_{ex}x_1} - 10^{-a_{ex}x_2})(10^{-a_{em}y_1} - 10^{-a_{em}y_2})}{\ln(10) a_{ex}a_{em}}$$  \hspace{1cm} (Eq. S5)

In this expression, $x_1$, $x_2$, $y_1$, and $y_2$ define the width and location of the excitation beam and the area seen by the detector (Figure S6b). For the instrument used, both of these cover the entire cuvette length. Thus $x_1$ and $y_1$ are equal to zero, and $x_2$ and $y_2$ are equal to the path length of the cuvette. In the interest of generality, this substitution will not be made until the final step.
The corrected intensity is what the intensity would be in the absence of the inner filter effects. This can be found by setting $\alpha_{ex}$ and $\alpha_{em}$ to zero in Equation S5 and integrating. Making this substitution yields the following.

$$I_{corr}(x, y) = \ln(10) I_{ex} \varepsilon_{F,ex} c_F \Phi_Q dx dy$$  \hspace{1cm} (Eq. S6)

$$I_{corr} = \ln(10) I_{ex} \varepsilon_{F,ex} c_F \Phi_Q (x_2 - x_1)(y_2 - y_1)$$  \hspace{1cm} (Eq. S7)

Dividing Equation S7 by Equation S5 and eliminating the common factor of $I_{ex} \varepsilon_{F,ex} c_F \Phi_Q$ gives the proper correction formula.

$$\frac{I_{corr}}{I_{obs}} = \frac{\ln(10)^2 \alpha_{ex}(x_2 - x_1) \alpha_{em}(y_2 - y_1)}{(10^{-\alpha_{ex}x_1} - 10^{-\alpha_{ex}x_2})(10^{-\alpha_{em}y_1} - 10^{-\alpha_{em}y_2})}$$  \hspace{1cm} (Eq. S8)

If the excitation beam width and the detector area both cover the entire cuvette length, then the equation becomes the expression of Equation S9.

$$\frac{I_{corr}}{I_{obs}} = \frac{\ln(10)^2 \alpha_{ex} L \alpha_{em} L}{(1 - 10^{-\alpha_{ex}L})(1 - 10^{-\alpha_{em}L})}$$  \hspace{1cm} (Eq. S9)

By cross-multiplying by $I_{obs}$ and noting that $\alpha_{ex/em}L = A_{ex/em}$, where $A_{ex/em}$ is the total absorbance of the solution at the excitation or emission wavelengths, Equation 1 of the main text is recovered.