Supporting information

Investigation of Regeneration Kinetics of Organic Dyes with Pyridine Ring Anchoring Group by Scanning Electrochemical Microscopy

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The diffusion flux from the solution bulk to the active electrode current is hindered by the insulating glass sheath and the presence of the sample. Normalized heterogeneous rate constant κ was extracted from experimental approach curves by fitting them with the model evaluated by Cornut and Lefrou.[1-5]

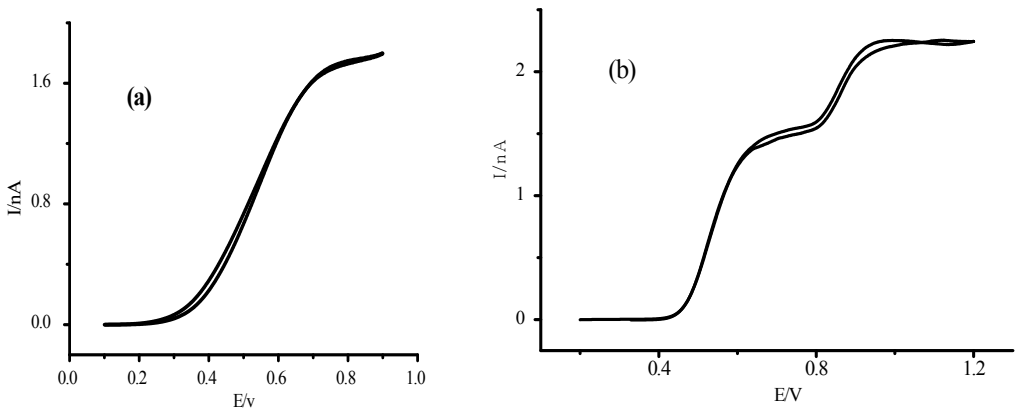

Fig.SI .1. Cyclic voltammogram of (a) 1mM T^- (b) 1mM LiI +0.1M LiTFS in acetonitrile solution at a Pt UME scan rate 0.05 V s^{-1}

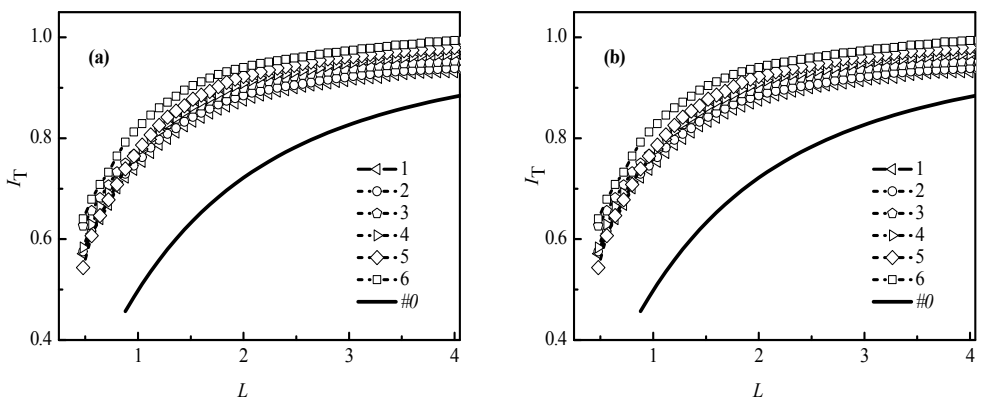

Fig. S2**.** (a) Normalized SECM feedback approach curves for the approach of a Pt disk UME towards a NiO/P1 film in the dark (curve #0) and under illumination by blue LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1} (1) 2.2, (2) 6.1, (3) 11.8, (4) 13.9, (5) 19.8, (6) 22.4. scan rate= 0.05 V s^{-1}, E_T = 0.7 V, electrolyte: 1 mM I^-. Heterogeneous rate constants k was obtained: (1) 0.009, (2) 0.013, (3) 0.025, (4) 0.036, (5) 0.05, (6) 0.099. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.134, (2) 0.193, (3) 0.372, (4) 0.535, (5) 0.788, (6) 1.473. (b) Photon flux density of red LED in 10^{-9} mol cm^{-2} s^{-1} (1) 4.19, (2) 6.81, (3) 9.44, (4) 12.06, (5) 13.11, (6) 14.68; the normalized rate constants k: (1) 0.0012, (2) 0.0021, (3) 0.0048, (4) 0.0076, (5) 0.0116, (6) 0.0167. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.0.431, (2) 0.531, (3) 0.0.621, (4) 0.709, (5) 0.733, (6) 0.804.

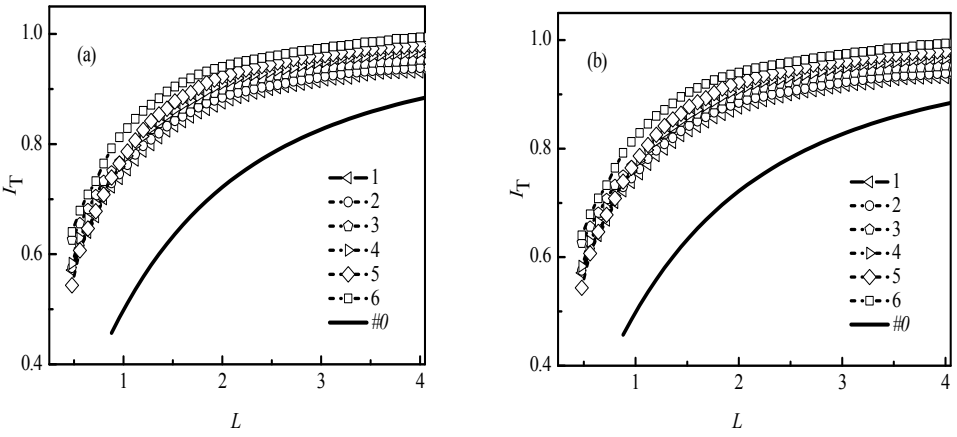

Fig. S3 (a) Normalized SECM feedback approach curves for the approach of a Pt disk UME towards a NiO/P1 film in the dark (curve #0) and under illumination by blue LED. Photon flux density of LED in $J_{hv}\times10^{-9}$ mol cm^{-2} s^{-1}:(1) 2.2, (2) 6.1, (3)11.8, (4) 13.9, (5) 19.8, (6) 22.4; scan rate= 0.05 V s^{-1}, E_T = 0.7 V, electrolyte: 1 mM I^-. First order kinetics of mediator recycling using normalized rate constants k: (1) 0.0434, (2) 0.0683, (3) 0.0737, (4) 0.0835, (5) 0.0864, (6) 0.1298. k_{eff} (10^{-3} cm s^{-1}): (1) 0.468, (2) 0.737, (3) 0.795, (4) 0.901, (5) 0.933, (6) 1.469. (b) Photon flux density of red LED in $J_{hv}\times10^{-9}$ mol cm^{-2} s^{-1}: (1) 4.19, (2) 6.81, (3) 9.44, (4) 12.06, (5) 13.11, (6) 14.68. The normalized rate constants k: (1) 0.0399, (2) 0.0491, (3)

0.0575, (4) 0.0657, (5) 0.0679, (6) 0.0745. k_{eff} (10^{-3} cm s^{-1}): (1) 0.431, (2) 0.531, (3) 0.621, (4) 0.709, (5) 0.733, (6) 0.804.

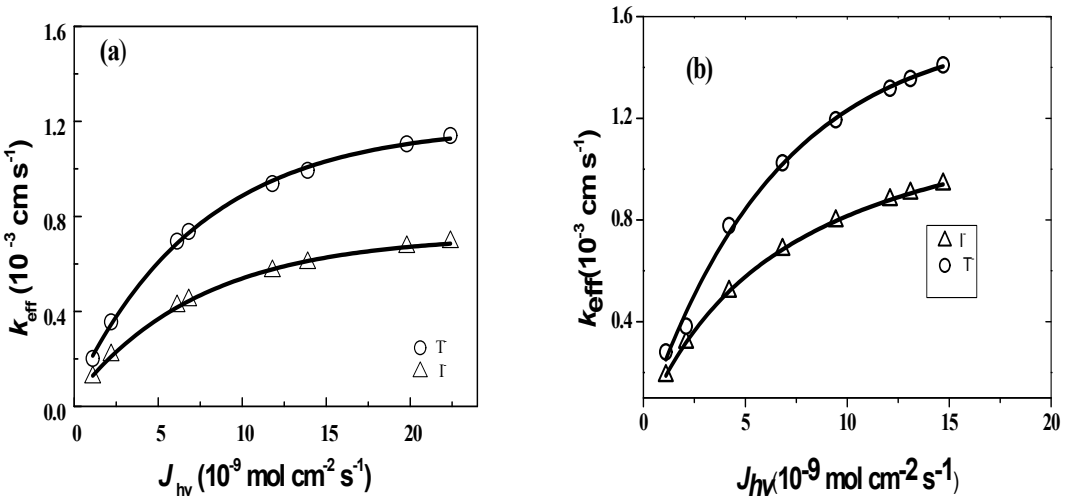

Fig. S4 Plots of experimental values of k_{eff} vs. J_{hv} for electrolytes (T^-) (○) and (I^-) (Δ) with (a) blue and (b) red LED.

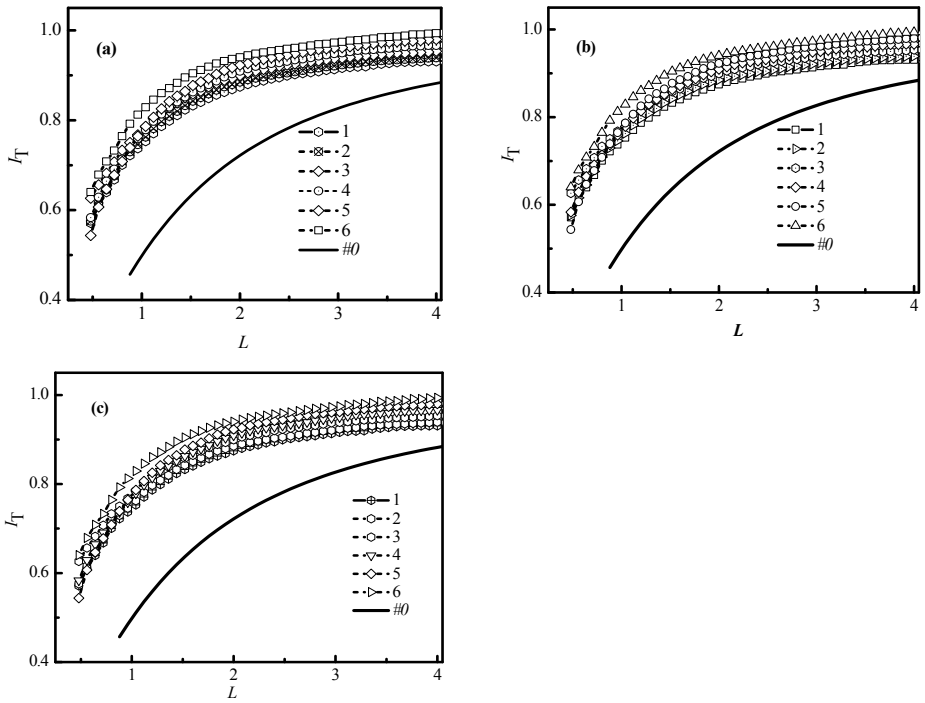

Fig. S5 (a) Normalized SECM feedback approach curves for the approach of a Pt disk UME towards a NiO/P1 film in the dark (curve #0) and under illumination by blue LED. Photon

flux density of LED in 10^{-9} mol cm^{-2} s^{-1}: (1) 2.2, (2) 6.1, (3) 11.8, (4) 13.9, (5) 19.8, (6) 22.4. scan rate=0.05 V s^{-1}, E_T = 0.7 V, electrolyte: 1 mM I^-. Solid lines are calculated curves for an approach of an UME towards an inert insulating surface (curve #0), and to samples with first order kinetics of mediator recycling using normalized rate constant *k*: (1) 0.0434, (2) 0.0683, (3) 0.0737, (4) 0.0835, (5) 0.0864, (6) 0.1298. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.2158, (2) 0.4222, (3) 0.4468, (4)0.5694, (5) 0.6041 (6) 0.6712. (b) NiO/CW2 film in under illumination by blue LED normalized rate constants *k*: (1) 0.0978, (2) 0.0995, (3) 0.1043, (4) 0.1095, (5) 0.1145 (6) 0.1212. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.145, (2) 0.148, (3) 0.155, (4) 0.162 (5) 0.171 (6) 0.182. (c) NiO/CW1 film in the dark (curve #0) and under illumination by blue LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1} normalized rate constants *k*: (1) 0.0621, (2) 0.0854 (3) 0.0894, (4) 0.0932, (5) 0.0973, (6) 0.1995. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.091, (2) 0.125, (3) 0.136 (4) 0.147, (5) 0.175, (6) 0.229.

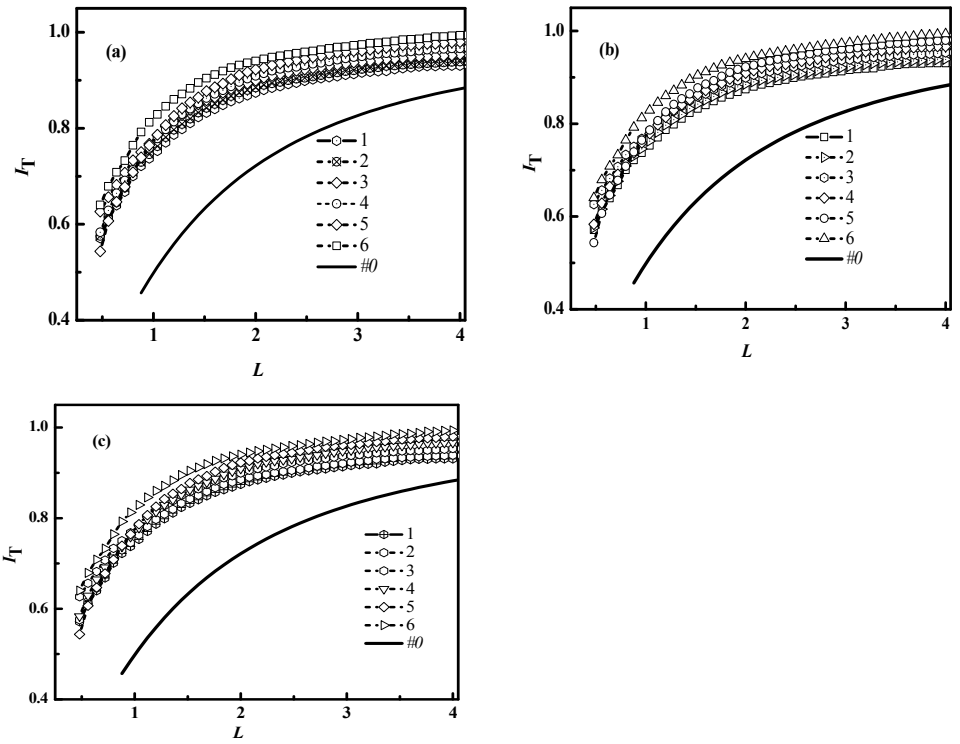

Fig. S6 Normalized SECM feedback approach curves for the approach of a Pt disk UME towards a NiO/P1 film in the dark (curve #0) and under illumination by red LED. (a) Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1} of normalized rate constants *k*: (1) 0.0012, (2) 0.0021, (3) 0.0048, (4) 0.0076, (5) 0.0116, (6) 0.0167. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.0477, (2) 0.0777, (3)

0.1024, (4) 0.1193, (5) 0.1317, (6) 0.1411. (b) NiO/CW1 film in the dark (curve #0) and under illumination by red LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1}, normalized rate constants *k*: (1) 0.0978, (2) 0.0995,(3) 0.1043,(4) 0.1095, (5) 0.1145, (6) 0.1212. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.0145, (2) 0.0148, (3) 0.0155, (4) 0.0162, (5) 0.0171, (6) 0.0182. (c) NiO/CW2 film in the dark (curve #0) and under illumination by red LED. Photon flux density in 10^{-9} mol cm^{-2} s^{-1}: (1) 4.19, (2) 6.81, (3) 9.44, (4) 12.06, (5) 13.11, (6) 14.68; normalized rate constants *k*: (1) 0.0375, (2) 0.0402, (3) 0.0464, (4) 0.0581, (5) 0.0614, (6) 0.0648. And k_{eff} (10^{-3} cm s^{-1}): (1) 0.054, (2) 0.059, (3) 0.069, (4) 0.086, (5) 0.091, (6) 0.096.

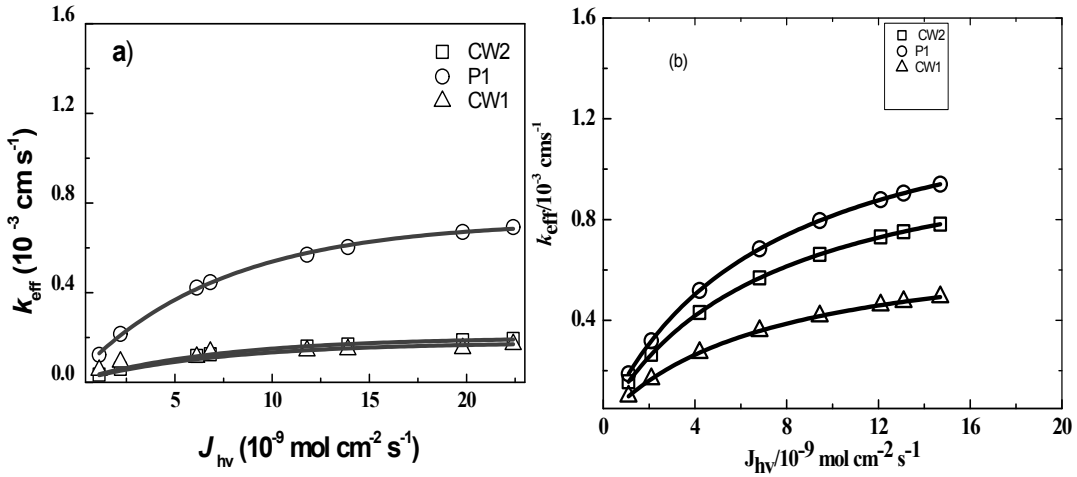

Fig. S7 Plot of experimental values of k_{eff} vs. J_{hv} (λ). (a) Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1} (1) 2.2, (2) 6.1, (3)11.8, (4) 13.9, (5) 19.8, (6) 22.4. Scan rate, 0.05Vs^{-1}, ET = 0.7 V, in electrolyte of 1mM (I^-), normalized rate constants *k* (1) 0.009, (2) 0.013, (3) 0.025, (4) 0.036, (5) 0.05, (6) 0.099. And k_{eff} $\times 10^{-3}$ cm s^{-1} (1) 0.216, (2) 0.422, (3) 0.446, (4) 0.569, (5) 0.604, (6) 0.671.For NiO/CW1 normalized rate constant *k* (1) 0.0978, (2) 0.0995, (3) 0.1043, (4) 0.1095, (5) 0.1145, (6) 0.1212. And k_{eff} $\times 10^{-3}$ cm s^{-1} (1) 0.0145, (2) 0.111, (3) 0.141, (4) 0.149, (5) 0.166 (6) 0.171. For NiO/CW2 LED Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1} (1) 4.19, (2) 6.81, (3) 9.44 (4) 12.06, (5) 13.11, (6) 14.68. Under illumination by red LED normalized rate constants *k* (1) 0.0978, (2) 0.0995, (3) 0.1043, (4) 0.1095, (5) 0.1145 (6) 0.1212. And k_{eff} $\times 10^{-3}$ cm s^{-1} (1) 0.145, (2) 0.148, (3) 0.155, (4) 0.162 (5) 0.171 (6) 0.182. (b) Photon flux density of red LED in 10^{-9} mol cm^{-2} s^{-1} (1) 4.19, (2) 6.81, (3) 9.44 (4) 12.06, (5) 13.11, (6) 14.68. Normalized rate constants for NiO/P1 *k* (1) 0.0012, (2) 0.0021, (3) 0.0048,

(4) 0.0076, (5) 0.0116, (6) 0.0167, and k_{eff} $\times 10^{-3}$ cm s^{-1} (1) 0.047, (2) 0.077, (3) 0.102, (4) 0.119, (5) 0.132, (6) 0.141. For the approach of a Pt disk UME towards a NiO/CW1 film in the dark (curve #0) and Normalized rate constants k (1) 0.0271, (2) 0.0331, (3) 0.0363, (4) 0.0391, (5) 0.0542, (6) 0.0598. And k_{eff} $\times 10^{-3}$ cm s^{-1} (1) 0.041, (2) 0.049, (3) 0.054, (4) 0.058, (5) 0.081, (6) 0.088. For NiO/CW2 film in the dark (curve #0) normalized rate constants k (1) 0.0375, (2) 0.0402 (3) 0.0464, (4) 0.0581, (5) 0.0614, (6) 0.0648. And k_{eff} $\times 10^{-3}$ cm s^{-1} (1) 0.056, (2) 0.059, (3) 0.069, (4) 0.086, (5) 0.091, (6) 0.096.

References

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