

Supporting Information

Surface Modification of Magnesium Ferrite Nanoparticles for Selective and Sustainable Remediation of Congo Red

Supawitch Hoijsang,^{a,b} Tanapong Kunakham,^b Jeeranan Nonkumwong,^c
Kajornsak Faungnawakij,^c Supon Ananta,^{d,f} Piyarat Nimmanpipug,^b
T. Randall Lee,^e and Laongnuan Srisombat^{b,f*}

^aGraduate School, Chiang Mai University, Chiang Mai 50200, Thailand

^bDepartment of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^cNational Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand

^dDepartment of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^eDepartment of Chemistry and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5003, United States

^fCenter of Excellence in Materials Science and Technology, Chiang Mai University, Chiang Mai 50200, Thailand

*Corresponding author.

Email address: laongnuan.sri@cmu.ac.th (L. Srisombat)

EXPERIMENTAL SECTION

Synthesis of Amine-Functionalized Magnesium Ferrite Nanoparticles (MgFe₂O₄-NH₂ NPs).

MgFe₂O₄-NH₂ NPs having ~90 nm diameters were synthesized by following our previous report.^{1,2} Generally, a mixture of 15 mmol of CH₃COONa and 10.0 mL of ethylene glycol was heated to 100 °C for 15 min. Subsequently, a solution containing 1 mmol of Mg(NO₃)₂·6H₂O, 2 mmol of Fe(NO₃)₃·9H₂O, and 5.0 mL of ethylene glycol was added into the heated mixture. The composite solution was continuously refluxed for 30 min followed by injection of 3.5 mL of ethanolamine. After heating the solution at 200 °C for 12 h, the mixture was allowed to cool to room temperature. The product was separated using an external magnet and washed with deionized water for several times and then ethanol. The black powder was dried at 70 °C overnight.

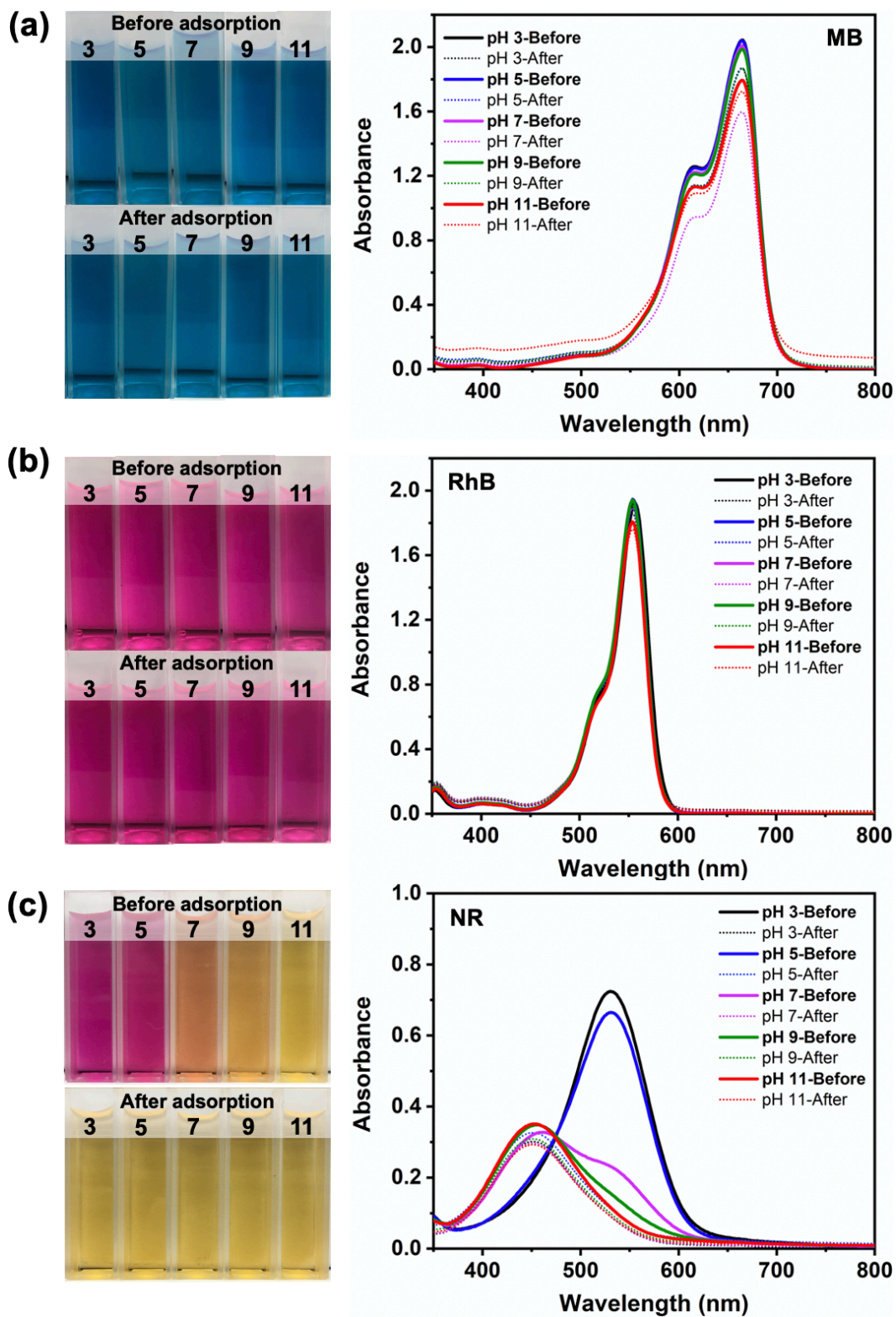


Figure S1. (left) Digital photos and (right) UV-Vis spectra of (a) MB, (b) RhB, (c) NR, (d) IC, (e) CR, and (f) MO in single-component solution systems of dyes before and after adsorption at pH 3–11.

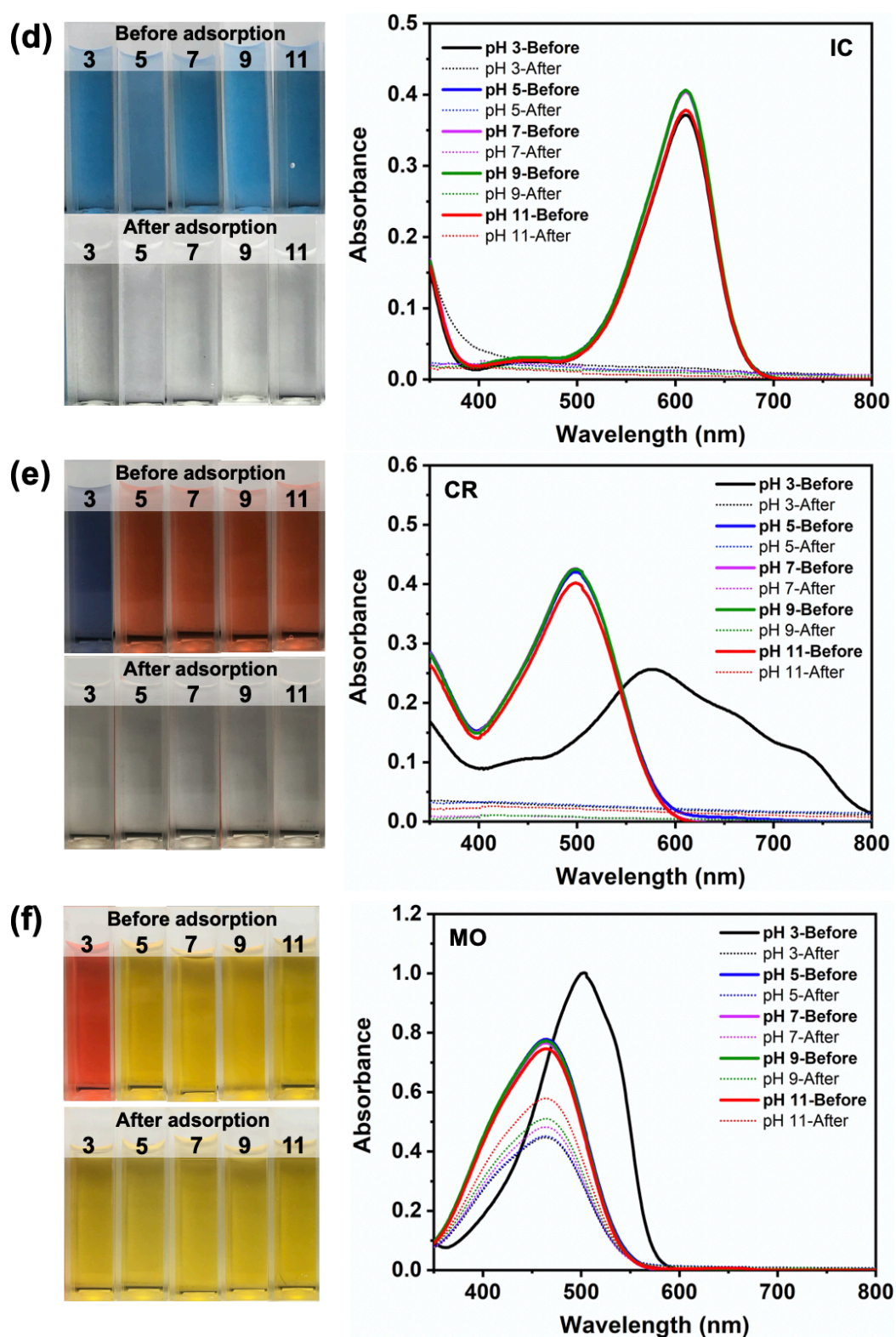


Figure S1. (cont.) (left) Digital photos and (right) UV-Vis spectra of (a) MB, (b) RhB, (c) NR, (d) IC, (e) CR, and (f) MO in single-component solution systems of dyes before and after adsorption at pH 3–11.

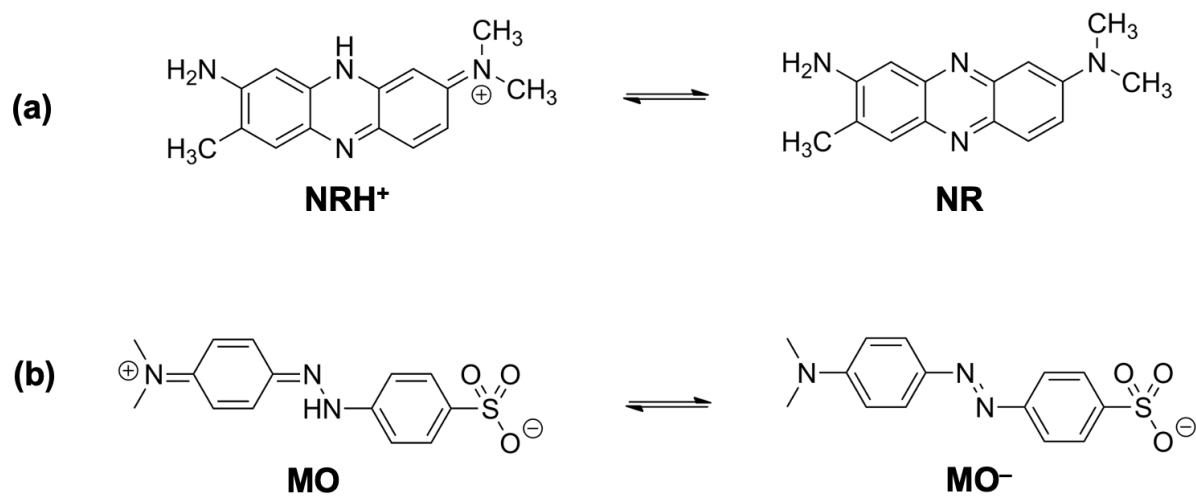


Figure S2. Chemical structures of (a) NR and (b) MO.

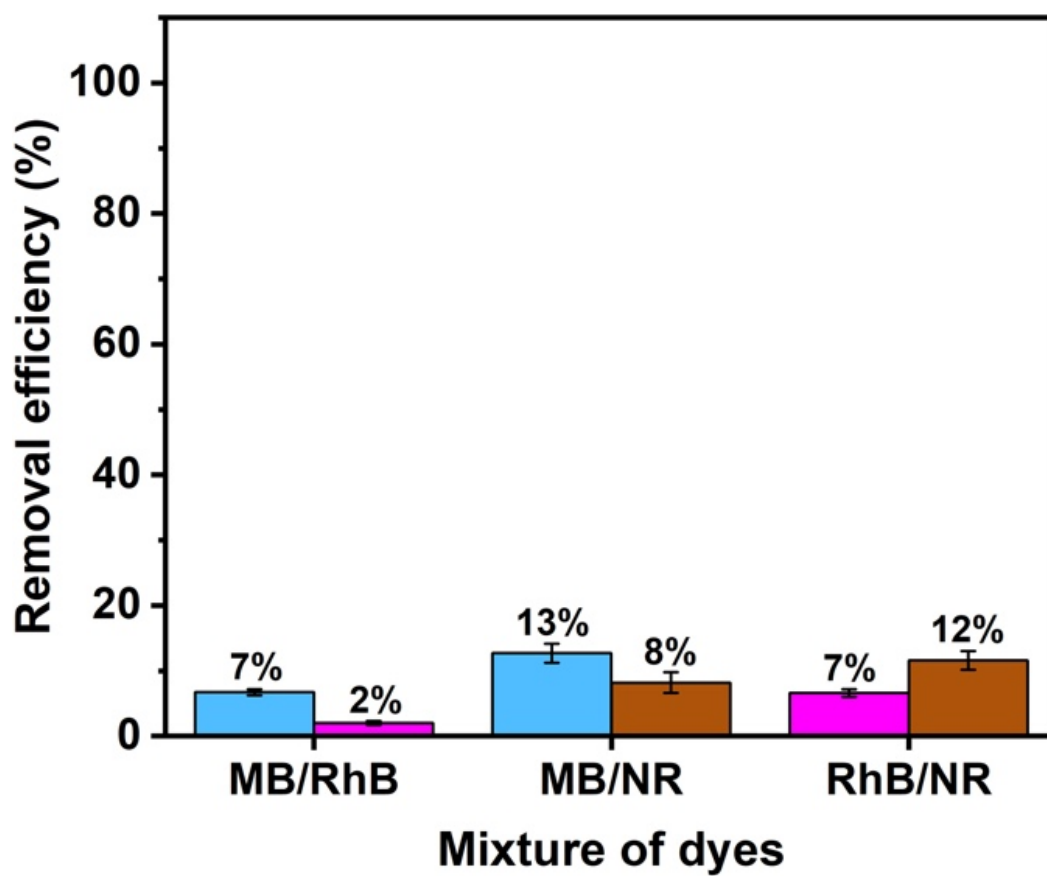


Figure S3. The relative removal efficiencies of dyes in cationic/cationic and cationic/neutral binary dye solutions at pH ~7.

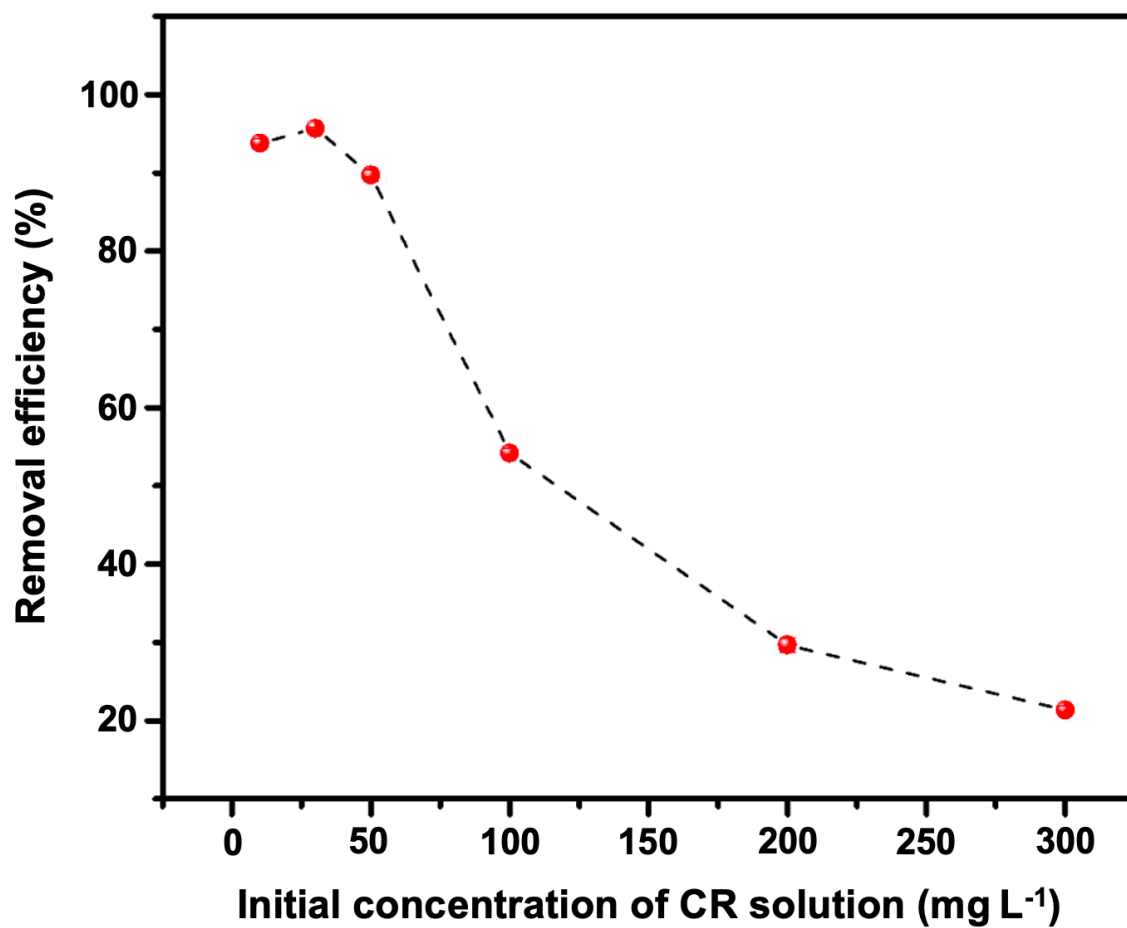


Figure S4. Effect of initial concentration of CR solution on the removal of CR by APTES-modified $\text{MgFe}_2\text{O}_4@\text{SiO}_2$ NPs at pH ~6.

Computational Simulations of the Dipole Moments and Nitrogen Atomic Charges of IC and CR Dyes

All computational calculations were performed using the Gaussian09 quantum chemical package³ and visualized using Gaussview. The geometry optimizations in vacuum for IC and CR were performed by using the density functional theory (DFT) hybrid functional B3LYP with 6-31G(d,p) basis set.^{4,5} The total energy, highest occupied molecular orbital (HOMO) energies, lowest unoccupied molecular orbital (LUMO) energies, dipole moment (μ) of the molecular system were calculated by using the same level of theory as the ground-state properties. The electronic structures were investigated according to natural bond orbitals (NBO) analysis. Chemical hardness (η) was estimated from the HOMO and LUMO frontier molecular orbitals following the equation below:

$$\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$$

where E_{HOMO} and E_{LUMO} is the HOMO and LUMO energies.

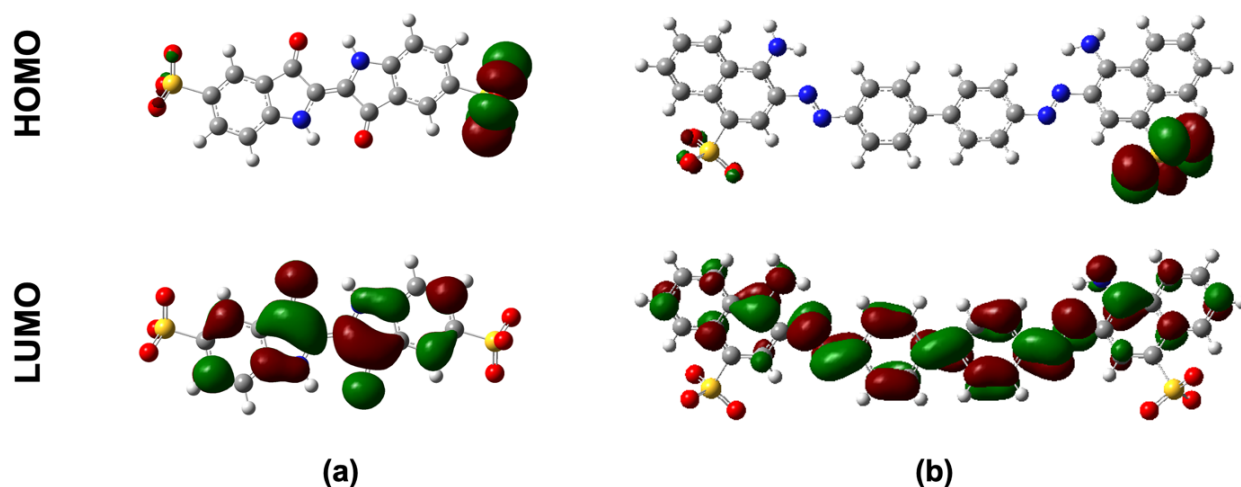


Figure S5. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) density of (a) IC and (b) CR molecules.

Table S1. Quantum Chemical Descriptors of IC and CR Dyes

Dye	E_{HOMO} (eV)	E_{LUMO} (eV)	η (eV)	μ (Debye)
IC	-0.0265	0.0548	0.0812	0.0012
CR	-0.0450	0.0358	0.0807	20.021

Table S2. Distribution of NBO Charges within Nitrogen-Containing Functional Groups Involved in Hydrogen Bonding in CR and IC from DFT Calculations

Dye: functional group	Atomic charge of N atom
IC: pyrrole N	-0.5850
	-0.5850
CR: amine N	-0.8446
	-0.8437
CR: azo N	-0.2342
	-0.2183
	-0.2343
	-0.2179

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