

Supplementary Material

Photophysical Properties of Donor-Acceptor Stenhouse Adducts and Their Inclusion Complexes with Cyclodextrins and Cucurbit[7]uril

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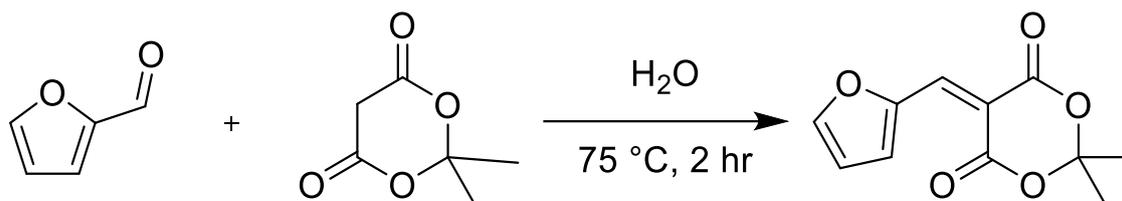
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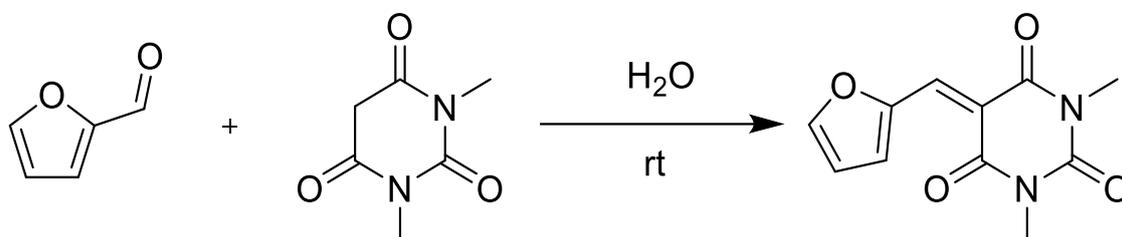
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1. Synthetic Methods



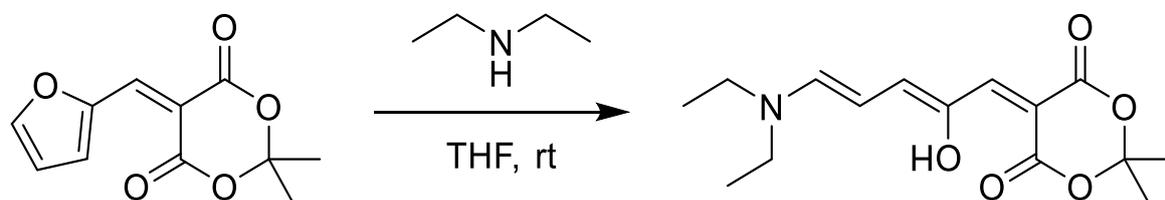
5-(Furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione:

2-Furaldehyde (3.3 mmol) was pipetted into 10 mL H₂O with stirring. Once mixed, 2,2-dimethyl-1,3-dioxane-4,6-dione (3.3 mmol) was added. The yellow mixture was heated to 75 °C for 2 hours while stirring gently. The faint yellow mixture transitioned to an opaque green-brown suspension. After cooling to room temperature, the brown precipitate was collected via vacuum filtration through a Whatman #1 filter paper. The product was washed with 50 mL H₂O to remove soluble impurities. This gave 2.3 mmol (70%) of 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione as a yellow-brown solid. NMR spectra match previously reported data [1].



5-(Furan-2-ylmethylene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione:

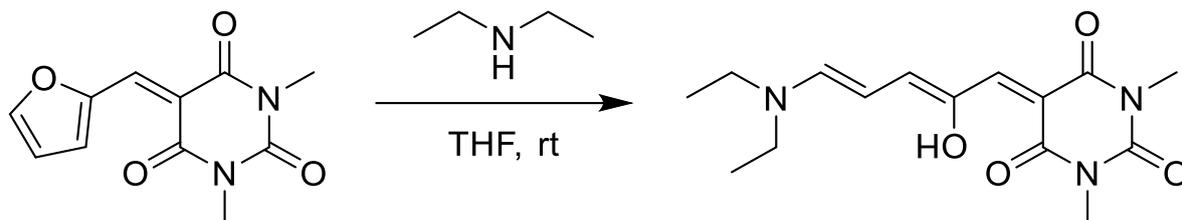
1,3-Dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (10 mmol) was added to 40 mL water and stirred. To this suspension was added 2-furaldehyde (10 mmol), and stirring was continued overnight at room temperature, forming a yellow precipitate. Vacuum filtration was used to collect the precipitated solid, which was then washed twice with 30 mL cold H₂O. The precipitate was dissolved in 75 mL dichloromethane and washed with 30 mL saturated aqueous NaHSO₃, 30 mL H₂O, 30 mL saturated aqueous NaHCO₃, and 30 mL brine. The organic phase was dried over MgSO₄, then gravity filtered. The solvent was stripped by rotary evaporation to give 8.6 mmol (86%) of 5-(furan-2-ylmethylene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione. NMR spectra match previously reported data [2].



5-((2Z,4E)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (DASA-M):

5-(Furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1.8 mmol) was added to 4.5 mL tetrahydrofuran and stirred. Diethylamine (1.8 mmol) was added dropwise, instantly giving an opaque magenta mixture. The mixture was stirred at room temperature for 10 minutes, then cooled in an ice bath for 20 minutes, causing a magenta precipitate to appear. The 5-((2Z,4E)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione was collected via vacuum filtration through a Whatman #1 filter paper and the retentate was washed with

60 mL ice-cold diethyl ether. This gave 0.83 mmol (46%) DASA-M. NMR spectra match previously reported data [3].



5-((2Z,4E)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (DASA-B):

5-(Furan-2-ylmethylene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (1.0 mmol) was added to 10 mL tetrahydrofuran and stirred. Diethylamine (1.0 mmol) was added to the suspension, and the solution rapidly became pink, then dark purple. The mixture was stirred at room temperature for 30 minutes. Cold *n*-hexane was added to the reaction mixture to precipitate 5-((2Z,4E)-5-(diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione, which was then obtained as dark purple crystals by vacuum filtration. This gave 0.67 mmol (67%) DASA-B. NMR spectra match previously reported data [4].

2. DASA Characterization

DASA-M

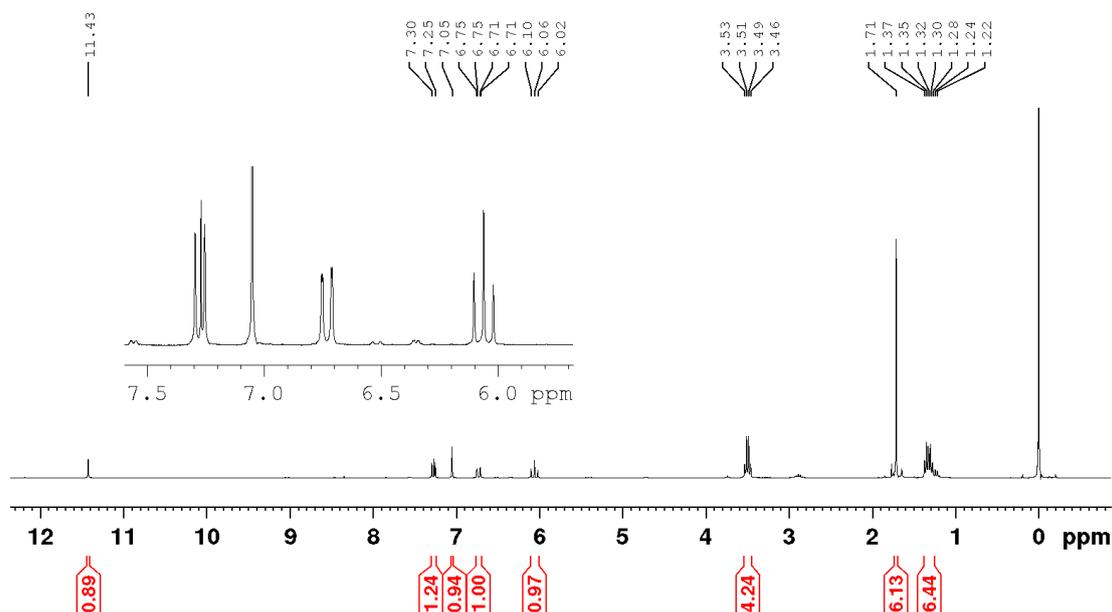


Figure S1. ^1H NMR spectrum of DASA-M.

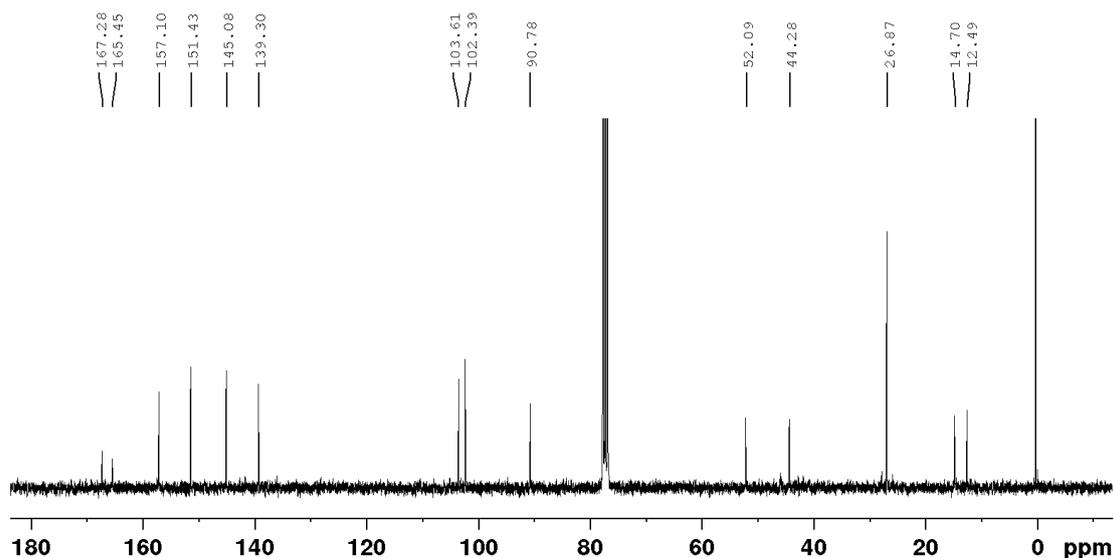


Figure S2. ^{13}C NMR spectrum of DASA-M.

^1H NMR (300 MHz, CDCl_3) δ 11.43 (s, 1H), 7.30-7.25 (d, $J = 12.3$ Hz, 1H), 7.05 (s, 1H), 6.75-6.71 (dd, $J = 12.43, 1.29$, 1H), 6.10-6.02 (t, $J = 12.35$, 1H), 3.53-3.46 (q, $J = 7.24$ Hz, 4H), 1.71 (s, 6H), 1.37-1.22 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.3, 165.5, 157.1, 151.4, 145.1, 139.3, 103.6, 102.4, 90.8, 52.1, 44.3, 26.87, 14.7, 12.5.

3. Fluorescence Enhancement of DASAs by CDs and CB[7]

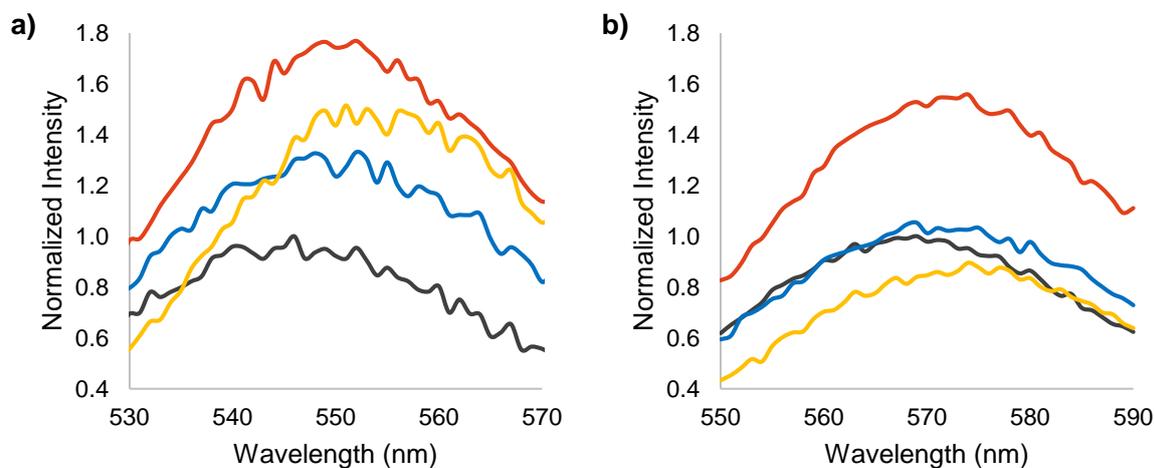


Figure S3. Normalized emission intensity of (a,b) DASA-M and DASA-B with no host (—), 20 mM HP- α -CD (—), 20 mM HP- β -CD (—), or 20 mM HP- γ -CD (—), showing that encapsulation by HP- γ -CD results in the greatest fluorescence enhancement for DASA-M and DASA-B.

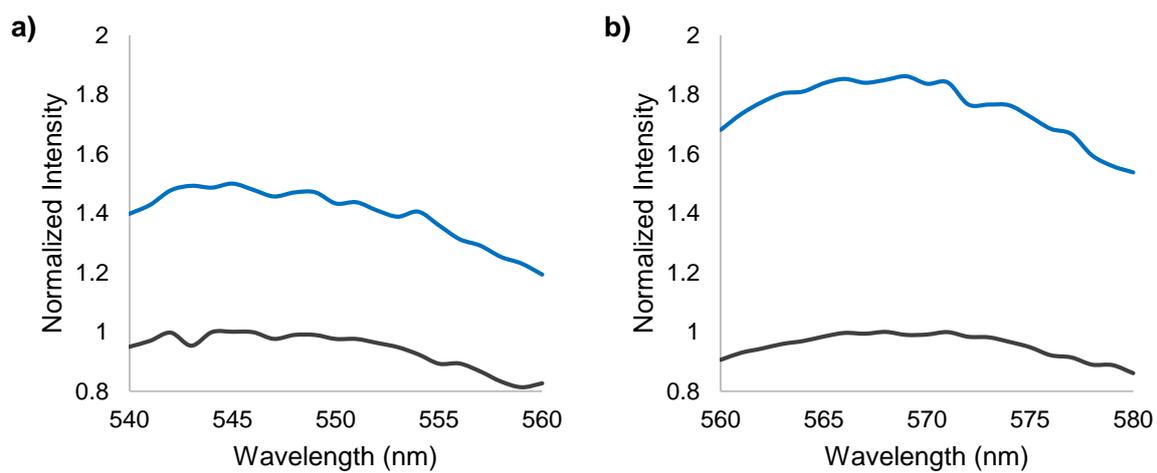


Figure S4. Normalized emission intensity of (a,b) DASA-M and DASA-B with no host (–) or 20 μM CB[7] (–).

4. Solvent- and Host-Based Negative Solvatochromism

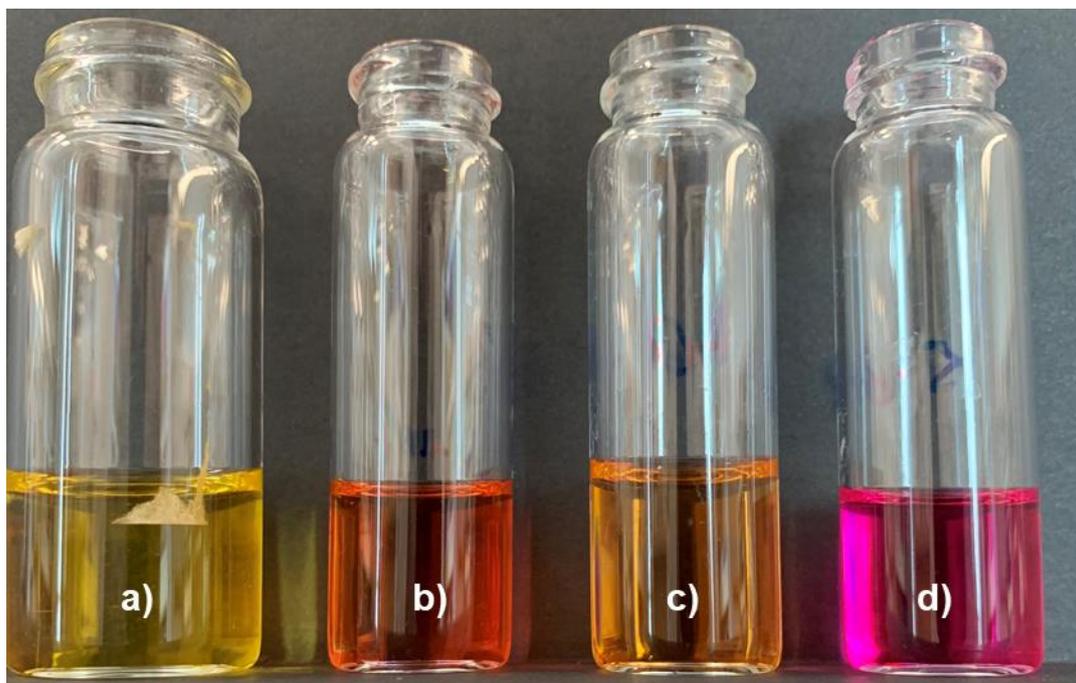


Figure S5. Solvent-based negative solvatochromism: (a) DASA-M in H₂O; (b) DASA-M in EtOH; (c) DASA-B in H₂O; (d) DASA-B in EtOH.

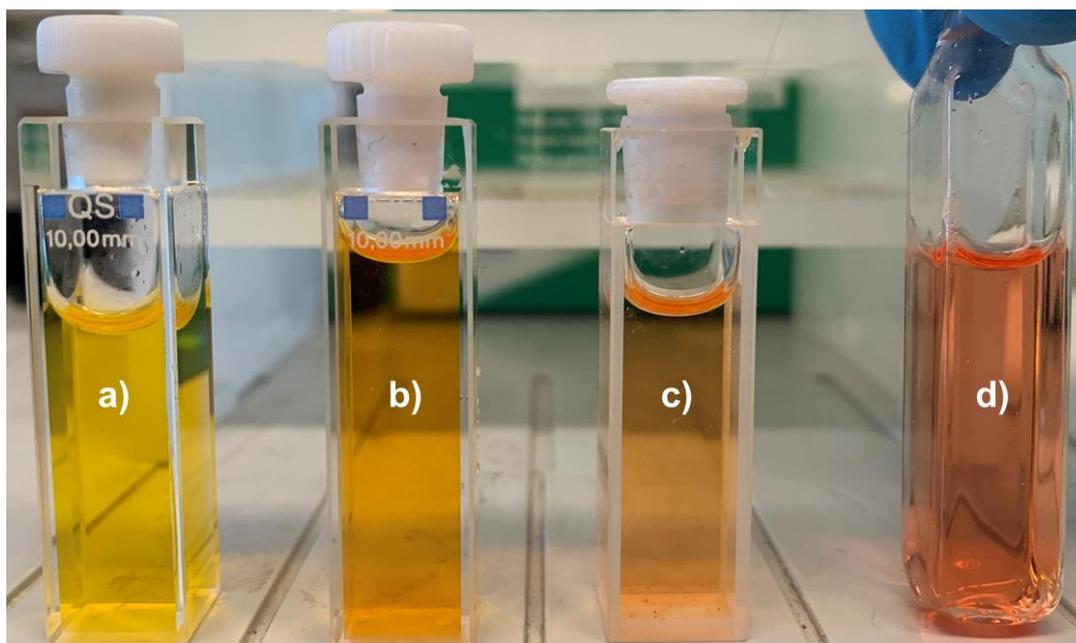


Figure S6. Host-based negative solvatochromism: (a) DASA-M in H₂O; (b) DASA-M in H₂O with 20 mM HP- γ -CD; (c) DASA-B in H₂O; (d) DASA-B with 20 mM HP- γ -CD in H₂O.

References

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