Supporting Information for

Engineering Central Substitutions in Heptamethine Dyes via Aryllithium Addition for Improved Fluorophore Performance

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Supplementary Figures

Figure S1 Synthetic methods for indolinium heptamethine cyanine (Cy7) fluorophores with modification on the methine linkage. (a-c) Synthesis of modified Cy7 dyes from custom Schiff bases (a),\(^1,2\) from Zincke salts (b),\(^3\) and from pyridinium benzoxazoles (c).\(^4\)

Figure S2 Structures of commercially-available or previously-reported heptamethine dyes in this work.
Figure S3 Normalized absorption and emission spectra of ethanol solution containing 2 μM (a) IR-780, (b) IR780-Ph, (c) IR780-Ph(Me), (d) IR780-Ph(CH₂OH), (e) IR780-Ph(OMe), (f) IR780-Ph(COOH), (g) IR780-Ph(CH₂StBu), (h) IR780-Ph(2Me), (i) IR780-Ph(OAllyl) and (j) IR780-Ph(2CH₂OH). Combined absorption and emission spectra are shown in (k) and (l), respectively.
Figure S4 Normalized absorption and emission spectra of water solution containing 2 μM (a) IR-780, (b) IR780-Ph, (c) IR780-Ph(CH₂OH), (d) IR780-Ph(2CH₂OH) and (e) IR780-Ph(COOH). Combined absorption and emission spectra are shown in (f) and (g), respectively.
Figure S5 Reduction of aggregation by 4'-aryl modifications. (a-d) Normalized absorption spectra of increasing concentrations of (a) IR-780, (b) IR780-Ph, (c) IR780-Ph(CH₂OH), and (d) IR780-Ph(2CH₂OH) in PBS. Absorbance smaller than 2 was measured through a 1 cm light path. Absorbance larger than 2 was measured through a 0.5 cm light path and doubled to represent absorbance at 1 cm.

Figure S6 Comparison of absorption spectra of dyes in 1:1 methanol/water for photobleach experiment and the spectrum of LED light source.
Figure S7 Absorption and emission of IR780-2C18 in different conditions. (a-b) Absorption (a) and emission (b) spectra of 2 μM IR780-2C18 in alcoholic solvents. (c-d) Absorption (c) and emission (d) spectra of IR780-2C18 in solvents with varying polarity. (e-f) Absorption (e) and emission (f) spectra of IR780-2C18 in ethanol with varying concentrations of HCl. (g-h) Absorption (g) and emission (h) spectra of IR780-Ph with varying concentrations of HCl for comparison. HCl stock solution (200 mM) was prepared by adding cold ethanol into acetyl chloride.
Figure S8 Comparison of membrane imaging using DiR and IR780-2C18. (a-b) Representative images of cell stained with 2.5 μM DiR (a) and IR780-2C18 (b). The brightness and contrast in (a) and (b) are adjusted to show the staining of the cell. Scale-bar: 20 μm. (c) Mean fluorescence intensity in A549 cells after incubation with 2.5 μM DiR or IR780-2C18 under same imaging condition after background subtraction. Data are calculated on 10 cells from four independent incubations for each dye. *** P≤0.001; two-tailed Student’s t-test.
**Table S1** Photophysical properties of Cy7 derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>λ&lt;sub&gt;max,abs&lt;/sub&gt; / nm</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt; / 10&lt;sup&gt;5&lt;/sup&gt; M&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;max,ems&lt;/sub&gt; / nm</th>
<th>Φ&lt;sub&gt;F&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>IR-780</td>
<td>Ethanol</td>
<td>784</td>
<td>2.17±0.03</td>
<td>806</td>
<td>0.208±0.007</td>
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<td></td>
<td>Water</td>
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<td>IR780-Ph</td>
<td>Ethanol</td>
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<td>2.37±0.05</td>
<td>784</td>
<td>0.37±0.02</td>
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<td>0.051±0.001</td>
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<tr>
<td>IR780-Ph(Me)</td>
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<td>764</td>
<td>2.73±0.07</td>
<td>787</td>
<td>0.37±0.03</td>
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<tr>
<td>IR780-Ph(CH&lt;sub&gt;2&lt;/sub&gt;OH)</td>
<td>Ethanol</td>
<td>765</td>
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<td></td>
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<td>1.18±0.03</td>
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<td>IR780-Ph(2Me)</td>
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<td>IR780-Ph(2CH&lt;sub&gt;2&lt;/sub&gt;OAllyl)</td>
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<td>2.34±0.04</td>
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<td>0.38±0.01</td>
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<td>IR780-Ph(2CH&lt;sub&gt;2&lt;/sub&gt;OH)</td>
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<td>0.39±0.01</td>
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<td></td>
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<td>IR780-Ph(2C18)</td>
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<td>790</td>
<td>0.180±0.004</td>
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<sup>a</sup> ICG in ethanol (Φ<sub>F</sub> = 0.132)<sup>5,6</sup> was used as a reference.

**Table S2** Absorption and emission maxima of 3a-d and their starting 4'-chloro dyes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ&lt;sub&gt;max,abs&lt;/sub&gt; / nm</th>
<th>λ&lt;sub&gt;max,ems&lt;/sub&gt; / nm</th>
<th>Compound</th>
<th>λ&lt;sub&gt;max,abs&lt;/sub&gt; / nm</th>
<th>λ&lt;sub&gt;max,ems&lt;/sub&gt; / nm</th>
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<tbody>
<tr>
<td>IR-775</td>
<td>785</td>
<td>812</td>
<td>3a [IR775-Ph(Me)]</td>
<td>764</td>
<td>785</td>
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<tr>
<td>IR-813</td>
<td>825</td>
<td>856</td>
<td>3b [IR813-Ph(Me)]</td>
<td>801</td>
<td>826</td>
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<tr>
<td>Chrom7</td>
<td>975</td>
<td>996</td>
<td>3c [Chrom7-Ph(Me)]</td>
<td>952</td>
<td>982</td>
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<tr>
<td>IR-1061</td>
<td>1058</td>
<td>n.d.&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3d [IR1061-Ph(Me)]</td>
<td>1040</td>
<td>n.d.&lt;sup&gt;a&lt;/sup&gt;</td>
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</tbody>
</table>

<sup>a</sup> Not determined due to fluorometer wavelength limit
Procedures and Characterization Methods

Materials
Indocyanine green (ICG) was purchased from Ambeed. DiR was purchased from MedChemExpress. DiI was purchased from AAT Bioquest. Hyclone calf serum was purchased from Cytiva and supplemented with 0.01% w/v NaN₃ as preservative. Preformed liposome in PBS (DPPC/CHOL 55:45 mol/mol, 60 mM total concentration) was prepared according to published procedure and diluted to desired concentration. HPLC grade solvents were used for all photophysical characterizations.

Dye handling and storage
All dyes were stored in pure solid form after purification in -20°C freezer. Stock solutions were prepared as 2 mM solutions in absolute ethanol and diluted into desired concentration for characterization.

Photophysical characterization
Absorption spectra were collected on a VWR UV-1600PC Scanning Spectrophotometer after blanking with the appropriate solvent. Photoluminescence spectra were obtained on a StellarNet SILVER-Nova spectrometer coupled with a Spectral Products ASTN-W100L-CM light source. Quartz or glass cuvettes (10 mm × 10 mm) or polystyrene cuvettes (10 mm × 5 mm) were used for absorption measurements. Quartz cuvettes (10 mm × 10 mm) were used for photoluminescence measurements. All spectra were obtained at ambient temperature. Fluorescence quantum yield was measured with 730 nm excitation using indocyanine green (ICG) in absolute ethanol as a reference (Φ_F = 0.132). Six or more data points were acquired for the calculation of absorption coefficient and quantum yield by linear regression, where the standard error of slopes of the unknowns were used to determine error values.

Stability assay in FBS
Dyes were diluted to 4 μM in 1 mL of bovine calf serum and placed in disposable cuvettes (10 mm × 5 mm). The cuvettes were sealed with Parafilm and placed in 37°C incubator for given time periods. Absorption spectra were taken using the maximum absorption to represent dye concentrations. For cysteine-reacted IR-780, the pristine IR-780 was pre-incubated in serum at 37°C for 1 h for the reaction to complete before starting the experiment. For IR-780, the incubation was carried out in 4 μM 250 μL solutions in microcentrifuge tubes, quenched until given time points with 800 μL cold methanol, cooled at -20°C for 30 min, centrifuged (1,7000×g, 5 min) to remove precipitated serum proteins, and measured on spectrometer. Each condition was performed in triplicate.

Photostability assay
Dyes were diluted to 4 μM in 1 mL of 1:1 methanol/water and placed in disposable cuvettes (10 mm × 5 mm). The cuvettes were illuminated through the 5 mm light path in front of a self-made LED light (LEDLightsWorld, 730 nm LED strips) matrix (6.8 mW/cm²) for given time periods. Absorption spectra were taken using the maximum absorption to represent the dye concentration.

Cell culture
A549 human lung cancer cell line (CCL-185, ATCC) was obtained from the American Type Culture Collection. T25 cell culture flask (Greiner Bio-One) was adopted to culture the A549 cells in DMEM cell culture medium (Corning) containing 1% Penicillin-Streptomycin (Pen Strep) (Gibco) and 10% fetal bovine serum (FBS)
(Gibco). To subculture cells, in a 35 mm Petri dish (Fisher Scientific), a 22 × 22 mm coverslip (Corning) was added, followed by adding cell suspension in 150 µL DMEM with 10% FBS and 1% Pen Strep to submerge the coverslip (2 mL). The Petri dish was left in the cell culture incubator at 37°C and 5% CO₂ for 48 hours before imaging.

**Fluorescence microscopy**

The Nikon Eclipse 80i upright microscope was used to perform the imaging in this study. The microscope was configured to epifluorescence mode and DIC mode. In epifluorescence mode, three sets of filters, Newport filter sets (HPF1425; exc/emi 710/800 nm), DAPI filter (Nikon V-2A; exc/emi 400/450 nm), and DiI filter (Nikon r-DiI; exc/emi 535/610 nm) were used. A mercury lamp, Nikon Intenslight C-HGFI lamp was used. In DIC mode, the sample was illuminated by a halogen lamp. Two Nomarski prisms, one polarizer, one analyzer, and one quarter-wave plate were used in the optical path. A DIC oil immersion condenser (numerical aperture (NA) 1.40) (Nikon D-CUO) and a 100X Plan Apo VC oil immersion objective (NA 1.40) (Nikon) was used in DIC mode. The images were collected by an EMCCD camera (iXonEM+Ultra897 BVF, Andor Technology). Images were recorded with a frame rate of 1 to 20 frames per second (fps).

For imaging of cell membrane, DiI staining medium with a final concentration of 5 µM was made by adding 1 µL of 5 mM DiI stock solution into 999 µL plain DMEM. **IR780-2C18** staining medium (final concentration 5 µM) was made by adding 2.5 µL of 2 mM IR780-2C18 stock solution to 997.5 µL of plain DMEM. Hoechst staining medium was made by adding 0.5 µL of 16.23 mM Hoechst stock solution into 1000 µL PBS (1:2000 dilution). The three dyes were mixed in a conical tube (VWR) to furnish the staining medium. Cells were washed once with PBS before incubating with the staining medium at 37°C and 5% CO₂ for 20 min before imaging.

Acquired images were analyzed with Fiji distribution of ImageJ. Pearson’s R value was calculated with the Coloc2 plugin. The brightness comparison between DiR and **IR780-2C18** was performed by calculating the absolute intensity, where the mean fluorescence intensity in cells and in the background were selected as ROIs and measured. The absolute intensity was calculated by subtracting the background from the cell fluorescence intensity.
Synthesis

Synthetic materials and methods

Unless otherwise noted, all commercial reagents were used without further purification. All reactions utilizing air- or moisture-sensitive reagents were performed under an atmosphere of dry N₂. Dry solvents were purchased from Thermo Scientific Chemicals and stored over sieves under an atmosphere of dry N₂. Chemical reagents were purchased from Ambeed, Oakwood Chemicals and Thermo Scientific Chemicals. Heptamethine dyes were purchased from Thermo Scientific Chemicals (IR-780, IR-775), TCI America (IR-813) and Enamine (IR-1061). Chrom7,¹¹ (2-bromobenzyl)(tert-butyl)sulfane,¹² and 2-bromo-1,3-benzenedimethanol,¹³ were synthesized according to published procedures.¹⁴

¹H NMR and ¹³C NMR spectra were collected in CDCl₃, CD₃CN or MeOD at 25 °C on Bruker 400 MHz or 500 MHz spectrometers at the NMR Facility at the Department of Chemistry and Biochemistry in the University of Arkansas, Fayetteville. All chemical shifts in ¹H NMR and ¹³C NMR are reported in the standard notation of ppm relative to residual solvent peak (CDCl₃ δH=7.26, δC=77.16; CD₃CN δH=1.94, δC=1.32; MeOD δH=3.31, δC=49.00; CD₂Cl₂ δH=5.32, δC=53.84). High resolution mass spectrometry was acquired on an IT-TOF (Shimadzu) at the University of Arkansas Statewide Mass Spectrometry Facility.

**((2-Bromo-3-methylbenzyl)oxy)trimethylsilane (S1):** To a flask containing 2-bromophenylmethanol (200 mg, 1.1 mmol) and triethylamine (0.22 mL, 1.6 mmol) dissolved in CH₂Cl₂ (10 mL) was added trimethylsilyl chloride (0.16 mL, 1.3 mmol). The mixture was stirred for 2.5 h at room temperature and concentrated to dryness. The crude product was separated by column chromatography (1:50 ethyl acetate/hexanes) to give S1 as a colorless liquid (274 mg, 99%), which is used without further purification. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 4.72 (s, 2H), 0.19 (s, 9H). This compound has also been characterized elsewhere.¹⁴

**1,3-Bis((allyloxy)methyl)-2-bromobenzene (S2):** To a flask containing 2-bromo-1,3-benzenedimethanol (305 mg, 1.41 mmol) and NaH (60% dispersion in mineral oil, 281 mg, 7.03 mmol) under N₂ was added dry DMF (7 mL). The reaction was stirred at room temperature for 0.5 h, followed by the dropwise addition of allyl bromide (0.35 mL, 4.2 mmol). The reaction was further stirred for 1 h, quenched with addition of MeOH and H₂O, and extracted into ethyl acetate. The organic layer was washed with H₂O (×4) and saturated NaCl, dried (Na₂SO₄) and concentrated. The crude product was separated by column chromatography (1:50 ethyl acetate/hexanes) to give S2 as a colorless liquid (417 mg, >99%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 4.72 (s, 2H), 0.19 (s, 9H). This compound has also been characterized elsewhere.¹⁴
4-Bromo-3,5-dimethyl-N,N-dioc-tadecylandiline (S3): To a microwave vessel containing 4-bromo-3,5-dimethylaniline (0.20 g, 1.0 mmol), 1-bromooctadecane (1.67 g, 5.0 mmol) and K$_2$CO$_3$ (0.55 g, 4.0 mmol) was added 15 mL of 1:2 H$_2$O/isopropanol. The reaction was carried out in a CEM Discover SP Microwave reactor at 120°C for 4h. The mixture was cooled, diluted with H$_2$O and extracted with CH$_2$Cl$_2$ ($\times$5), dried (Na$_2$SO$_4$) and concentrated. The crude product was separated by column chromatography (hexanes) to give S3 as a white solid (481 mg, 68%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.38 (s, 2H), 3.20 (t, $J$ = 7.6 Hz, 4H), 2.36 (s, 6H), 1.60 – 1.51 (m, 4H), 1.36 – 1.22 (m, 64H), 0.90 (t, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.12, 138.48, 113.07, 112.27, 51.23, 32.11, 29.88, 29.80, 29.53, 27.38, 27.34, 24.49, 22.85, 14.24. HRMS (ESI$^+$) calcd 704.5703, found 704.5695 for C$_{44}$H$_{83}$BrN$^+$ (M+H$^+$).

2,6-Bis(2-(3,3-dimethyl-1-propylindolin-2-ylidene)ethylidene)cyclohexan-1-one (IR780=O): To a flask containing IR-780 iodide (500 mg, 0.75 mmol) and sodium acetate (184 mg, 2.25 mmol) was added dry DMF (10 mL) followed by three freeze-pump-thaw cycles. The reaction was then stirred at 80°C under N$_2$ for 3 h. The mixture was diluted in ethyl acetate, washed with H$_2$O ($\times$4) and saturated NaCl, dried (Na$_2$SO$_4$) and concentrated. The crude product was separated by column chromatography (1:7.5 ethyl acetate/hexanes) to give IR-780=O as a dark red solid (365 mg, 93%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 13.2 Hz, 2H), 7.26 – 7.13 (m, 4H), 6.90 (t, $J$ = 7.4 Hz, 2H), 6.68 (d, $J$ = 8.0 Hz, 2H), 5.46 (d, $J$ = 13.2 Hz, 2H), 3.64 (t, $J$ = 7.4 Hz, 2H), 2.61 (t, $J$ = 6.2 Hz, 4H), 1.91 – 1.83 (m, 2H), 1.76 (h, $J$ = 7.5 Hz, 4H), 1.67 (s, 12H), 1.01 (t, $J$ = 7.4 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.45, 162.51, 144.48, 139.77, 132.97, 127.68, 126.58, 121.84, 120.48, 106.81, 92.63, 46.63, 44.21, 28.88, 25.93, 22.68, 19.84, 11.84. HRMS (ESI$^+$) calcd 521.3526, found 521.3530 for C$_{36}$H$_{45}$N$_2$O$^+$ (M+H$^+$).

**General procedure A: preparation of heptamethine=O.** The preparation is adapted from previous reports.$^{15,16}$ Specifically, heptamethine-Cl (1.0 equiv.), N-hydroxysuccinimide (NHS, 3.0 equiv.) and N,N-diisopropylethylamine (3.0 equiv.) were dissolved in DMF and stirred at room temperature until complete conversion of the starting heptamethine-Cl as determined by TLC. The mixture was then diluted in ethyl acetate, washed with H$_2$O ($\times$4) and saturated NaCl, dried (Na$_2$SO$_4$) and concentrated. The crude product was separated by column chromatography (1:200 methanol/CH$_2$Cl$_2$) to give heptamethine=O.
2,6-Bis(2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohexan-one (IR775=O): Following General Procedure A, IR-775 chloride (50 mg, 0.096 mmol) was reacted with NHS (33 mg, 0.29 mmol) and DIPEA (50 μL, 0.29 mmol) in dry DMF (2 mL) for 18 h to give IR775=O as a dark red-orange solid (31 mg, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, $J = 13.2$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 4H), 6.90 (t, $J = 7.4$ Hz, 2H), 6.68 (d, $J = 7.9$ Hz, 2H), 5.41 (d, $J = 13.2$ Hz, 2H), 3.21 (s, 6H), 2.62 (t, $J = 6.2$ Hz, 4H), 1.87 (p, $J = 6.4$ Hz, 2H), 1.68 (s, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 186.60, 163.33, 144.68, 139.70, 132.91, 127.73, 126.93, 121.80, 120.59, 106.52, 92.65, 46.52, 29.36, 28.78, 25.95, 22.63. HRMS (ESI$^+$) calcd 465.2900, found 465.2928 for C$_{32}$H$_{37}$N$_2$O$^+$ (M+H$^+$).

2,6-Bis(2-(1,1,3-trimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)ethylidene)cyclohexan-one (IR813=O): Following General Procedure A, IR-813 p-toluenesulphonate (100 mg, 0.152 mmol) was reacted with NHS (46 mg, 0.40 mmol) and DIPEA (69 μL, 0.40 mmol) for 1 h to give IR813=O as a deep red to dark magenta solid (39.5 mg, 54%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.37 (d, $J = 13.2$ Hz, 2H), 8.07 (d, $J = 8.6$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.8$ Hz, 2H), 7.50 (ddd, $J = 8.3$, 6.7, 1.3 Hz, 2H), 7.33 – 7.25 (m, 2H), 7.10 (d, $J = 8.7$ Hz, 2H), 5.48 (d, $J = 13.3$ Hz, 2H), 3.33 (s, 6H), 2.69 (t, $J = 5.5$ Hz, 4H), 2.04 (s, 12H), 1.97 – 1.90 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 186.53, 165.26, 141.92, 132.81, 130.04, 129.85, 129.82, 129.48, 129.07, 126.93, 126.81, 122.60, 121.93, 109.10, 92.37, 48.54, 29.61, 28.05, 25.99, 22.69. HRMS (ESI$^+$) calcd 565.3213, found 565.3235 for C$_{40}$H$_{41}$N$_2$O$^+$ (M+H$^+$).

2,6-Bis(2-(2-(tert-butyl)-7-(dimethylamino)-4H-chromen-4-ylidene)ethylidene)cyclohexan-one (Chrom7=O): Following General Procedure A, Chrom7 chloride (40 mg, 0.061 mmol) was reacted with NHS (23 mg, 0.20 mmol) and DIPEA (32 μL, 0.18 mmol) for 2 h to give Chrom7=O as a dark purple solid (10 mg, 28%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J = 12.8$ Hz, 2H), 7.63 (d, $J = 9.0$ Hz, 2H), 6.58 (dd, $J = 9.0$, 2.6 Hz, 2H), 6.49 (s, 2H), 6.39 – 6.28 (m, 4H), 3.01 (s, 12H), 2.74 (t, $J = 5.9$ Hz, 4H), 1.87 (p, $J = 5.9$ Hz, 2H), 1.28 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.37, 154.01, 152.03, 135.45, 131.76, 130.44, 123.79, 111.21, 109.88, 104.82, 98.94, 97.89, 40.36, 35.86, 28.18, 26.66, 22.69. HRMS (ESI$^+$) calcd 605.3738, found 605.3730 for C$_{40}$H$_{49}$N$_2$O$_3^+$ (M+H$^+$).
2,6-Bis(2-(2,6-diphenyl-4H-thiopyran-4-ylidene)ethylidene)cyclohexan-1-one (IR1061=O): Following General Procedure A, IR-1061 tetrafluoroborate (95 mg, 0.13 mmol) was reacted with NHS (48 mg, 0.42 mmol) and DIPEA (66 μL, 0.38 mmol) for 2 h to give IR1061=O as a dark brown solid (50 mg, 61%).\(^\text{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \(J = 12.8\) Hz, 2H), 7.69 – 7.53 (m, 8H), 7.50 – 7.36 (m, 14H), 6.86 (s, 2H), 6.08 (d, \(J = 13.0\) Hz, 2H), 2.68 (t, \(J = 6.0\) Hz, 4H), 1.85 (p, \(J = 6.0\) Hz, 2H).\(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 187.77, 140.00, 139.87, 137.99, 137.64, 137.58, 132.49, 130.76, 129.66, 129.43, 129.06, 126.43, 126.37, 126.13, 119.57, 118.58, 26.58, 22.30. HRMS (ESI\(^+\)) calcd 643.2124, found 643.2086 for \(C_{44}H_{35}OS_2\)\(^+\) (M+H\(^+\)).

**General procedure B: preparation of meso-substituted heptamethine dyes.** Unless otherwise noted, aryl bromide (0.51 mmol) was dissolved in dry THF (1 mL) and cooled to -84 °C. To this solution was added \(n\)-BuLi (2.3 M in cyclohexane/hexanes, 147 μL, 0.34 mmol). The mixture was stirred for 10 min at this temperature. A red to orange solution of keto-heptamethine (0.042 mmol) in dry THF (1 mL) was added dropwise. The mixture was allowed to warm up to room temperature and stirred for 30 min. The yellow or orange reaction mixture was quenched by adding 1:10 HCl which resulted in a rapid color change into dark green. The mixture was diluted in H\(_2\)O and extracted with CH\(_2\)Cl\(_2\) (×4) and dried (Na\(_2\)SO\(_4\)). The crude product was purified by column chromatography (1:30 to 1:20 methanol / CH\(_2\)Cl\(_2\)).

2-(2-(6-(2-(3,3-Dimethyl-1-propylindolin-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride (IR780-Ph): Following General Procedure B, IR780=O (22 mg, 0.042 mmol) was reacted with bromobenzene (80 mg, 0.51 mmol) and \(n\)-BuLi (2.3 M, 0.15 mL, 0.34 mmol) to give IR780-Ph as a green solid (27 mg, >99%).\(^{1}H\) NMR (400 MHz, MeOD with a few drops of CDCl\(_3\)) \(\delta\) 7.65 – 7.52 (m, 3H), 7.33 (td, \(J = 7.6, 1.2\) Hz, 2H), 7.29 – 7.21 (m, 6H), 7.16 (t, \(J = 7.0\) Hz, 4H), 6.11 (d, \(J = 14.0\) Hz, 2H), 4.01 (t, \(J = 7.3\) Hz, 4H), 2.70 (t, \(J = 6.3\) Hz, 4H), 2.07 (p, \(J = 6.3\) Hz, 2H), 1.84 (h, \(J = 7.4\) Hz, 4H), 1.17 (s, 12H), 1.02 (t, \(J = 7.4\) Hz, 6H).\(^{13}C\) NMR (101 MHz, MeOD with a few drops of CDCl\(_3\)) \(\delta\) 172.91, 163.77, 149.34, 143.28, 141.61, 139.86, 132.19, 130.32, 129.50, 129.41, 129.13, 125.68, 122.94, 111.40, 100.49, 49.53, 46.22, 28.03, 25.43, 22.10, 21.45, 11.76. HRMS (ESI\(^+\)) calcd 581.3890, found 581.3887 for \(C_{42}H_{49}N_2\)\(^+\) (M\(^+\)).
2-(2-(6-(2-(3,3-Dimethyl-1-propyldinolin-2-ylidene)ethylidene)-2'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride [IR780-Ph(Me)]: Following General Procedure B, IR780=O (22 mg, 0.042 mmol) was reacted with 2-bromotoluene (87 mg, 0.51 mol) and n-BuLi (2.3 M, 0.15 mL, 0.34 mmol) to give IR780-Ph(Me) as a green solid film (23 mg, 93%). $^1$H NMR (400 MHz, MeOD) $\delta$ 7.51 – 7.40 (m, 4H), 7.39 – 7.28 (m, 4H), 7.25 – 7.15 (m, 6H), 7.09 (d, $J = 7.3$ Hz, 1H), 6.19 (d, $J = 14.0$ Hz, 2H), 4.05 (t, $J = 7.3$ Hz, 4H), 2.73 (t, $J = 6.3$ Hz, 4H), 2.14 (s, 2H), 2.07 (p, $J = 6.2$ Hz, 2H), 1.83 (h, $J = 7.4$ Hz, 4H), 1.16 (s, 6H), 1.13 (s, 6H), 1.01 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (101 MHz, MeOD) $\delta$ 172.05, 161.89, 147.06, 142.37, 140.75, 138.23, 135.93, 130.43, 130.33, 129.15, 128.37, 126.11, 124.61, 121.97, 115.00, 110.49, 99.57, 53.48, 48.52, 45.00, 26.86, 26.66, 24.12, 21.22, 20.35, 10.33. HRMS (ESI$^+$) calcd 595.4048, found 595.4047 for C$_{43}$H$_{51}$N$_2$O$^+$ (M$^+$).

2-(2-(6-(2-(3,3-Dimethyl-1-propyldinolin-2-ylidene)ethylidene)-2'(hydroxymethyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride [IR780-Ph(CH$_2$OH)]: Following General Procedure B, IR780=O (22 mg, 0.042 mmol) was reacted with ((2-bromo-3-methylbenzyl)oxy)trimethylsilane (131 mg, 0.51 mol) and n-BuLi (2.3 M, 0.15 mL, 0.34 mmol) to give IR780-Ph(CH$_2$OH) as a green solid film (21 mg, 78%). $^1$H NMR (400 MHz, MeOD) $\delta$ 7.80 (d, $J = 7.7$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.38 – 7.29 (m, 4H), 7.27 – 7.14 (m, 6H), 7.11 (d, $J = 7.4$ Hz, 1H), 6.19 (d, $J = 14.1$ Hz, 2H), 4.45 (s, 2H), 4.05 (t, $J = 7.4$ Hz, 4H), 2.73 (s, 4H), 2.07 (p, $J = 6.5$ Hz, 2H), 1.82 (h, $J = 7.5$ Hz, 4H), 1.17 (s, 6H), 1.14 (s, 6H), 1.01 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (101 MHz, MeOD) $\delta$ 173.52, 148.67, 143.74, 142.21, 141.13, 137.89, 132.04, 130.54, 129.76, 129.67, 128.60, 128.49, 125.94, 123.30, 111.83, 101.01, 62.00, 49.93, 46.34, 28.27, 28.02, 25.52, 22.59, 21.72, 11.65. HRMS (ESI$^+$) calcd 611.3996, found 611.4005 for C$_{43}$H$_{51}$N$_2$O$^+$ (M$^+$).

2-(2-(6-(2-(3,3-Dimethyl-1-propyldinolin-2-ylidene)ethylidene)-2'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride [IR780-Ph(OMe)]: Following General Procedure B, IR780=O (22 mg, 0.042 mmol) was reacted with 2-bromoanisole (95 mg, 0.51 mol) and n-BuLi (2.3 M, 0.15 mL, 0.34 mmol) to give IR780-Ph(OMe) as a green solid film (25 mg, 98%). $^1$H NMR (400 MHz, MeOD) $\delta$ 7.59 (t, $J = 8.0$ Hz, 1H), 7.38 – 7.26 (m, 7H), 7.25 – 7.13 (m, 5H), 7.08 (dd, $J = 7.4$, 1.7 Hz, 1H), 6.16 (d, $J =$...
14.1 Hz, 2H), 4.04 (t, J = 7.4 Hz, 4H), 3.75 (s, 3H), 2.70 (s, 4H), 2.14 – 2.06 (m, 2H), 1.82 (h, J = 7.5 Hz, 4H), 1.21 (s, 6H), 1.16 (s, 6H), 1.02 (t, J = 7.4 Hz, 6H). 13C NMR (101 MHz, MeOD) δ 172.92, 157.89, 148.61, 143.81, 142.08, 131.93, 131.32, 129.67, 128.43, 125.80, 123.30, 122.10, 112.60, 111.72, 100.81, 56.27, 49.81, 46.28, 28.16, 27.96, 25.56, 22.47, 21.69, 11.67. HRMS (ESI⁺) calcld 611.3996, found 611.4004 for C_{43}H_{51}N_{2}O⁺ (M⁺).

2-(2′-Carboxy-6-(2-(3,3-dimethyl-1-propylindolin-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1′-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-iium chloride [IR780-Ph(COOH)]: Following General Procedure B, IR780=O (22 mg, 0.042 mmol) was reacted with tert-butyl 2-bromobenzoate (130 mg, 0.51 mol) and n-BuLi (2.3 M, 0.15 mL, 0.34 mmol) to give IR780-Ph(COOH) as a green solid (13 mg, 50%). 1H NMR (400 MHz, MeOD) δ 8.20 (d, J = 7.7 Hz, 1H), 7.70 (dt, J = 27.0, 7.6 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.26 – 7.11 (m, 7H), 6.15 (d, J = 14.0 Hz, 2H), 4.02 (t, J = 7.3 Hz, 4H), 2.70 (t, J = 6.2 Hz, 4H), 2.17 – 1.96 (m, 2H), 1.81 (h, J = 7.4 Hz, 4H), 1.19 (s, 6H), 1.12 (s, 6H), 1.00 (t, J = 7.4 Hz, 6H). 13C NMR (101 MHz, MeOD) δ 172.97, 164.94, 148.86, 143.83, 142.12, 141.00, 132.65, 132.58, 132.15, 131.90, 129.63, 125.73, 123.28, 111.65, 100.71, 49.80, 46.24, 28.30, 27.97, 25.78, 22.30, 21.66, 11.64. HRMS (ESI⁺) calcld 625.3789, found 625.3784 for C_{43}H_{49}N_{2}O_{2}⁺ (M⁺).

2-(2′-(tert-Butylthio)methyl)-6-(2-(3,3-dimethyl-1-propylindolin-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1′-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-iium chloride [IR780-Ph(CH_{3}StBu)]: Following General Procedure B, IR780=O (22 mg, 0.042 mmol) was reacted with (2-bromobenzyl)(tert-butyl)sulfane (133 mg, 0.51 mol) and n-BuLi (2.3 M, 0.15 mL, 0.34 mmol) to give IR780-Ph(CH_{3}StBu) as a green solid film (29 mg, 95%). 1H NMR (400 MHz, MeOD) δ 7.62 (dd, J = 7.6, 1.5 Hz, 1H), 7.51 (dt, J = 19.7, 7.4, 1.5 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.29 – 7.10 (m, 7H), 6.20 (d, J = 14.1 Hz, 2H), 4.07 (t, J = 7.3 Hz, 4H), 3.63 (s, 2H), 2.85 – 2.64 (m, 4H), 2.18 – 2.00 (m, 2H), 1.83 (h, J = 7.4 Hz, 4H), 1.28 – 1.21 (m, 15H), 1.17 (s, 6H), 1.01 (t, J = 7.4 Hz, 6H). 13C NMR (101 MHz, MeOD) δ 173.51, 161.64, 149.13, 143.75, 142.19, 139.52, 138.01, 132.81, 131.83, 131.20, 129.90, 129.66, 128.44, 125.94, 123.30, 111.83, 100.97, 49.98, 46.33, 43.71, 31.16, 30.94, 28.50, 28.05, 25.69, 22.62, 21.74, 11.67. HRMS (ESI⁺) calcld 683.4393, found 683.4369 for C_{47}H_{59}N_{2}S⁺ (M⁺).
1,3,3-Trimethyl-2-(2-(2'-methyl-6-(2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3H-indol-1-ium chloride [(IR775-Ph(Me)]: Following General Procedure B, IR775=O (18 mg, 0.038 mmol) was reacted with 2-bromotulene (78 mg, 0.46 mmol) and n-BuLi (2.3 M, 0.13 mL, 0.31 mmol) to give IR775-Ph(Me) as a green solid (17 mg, 80%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 – 7.27 (m, 5H), 7.19 – 7.02 (m, 9H), 6.07 (d, \(J = 14.0\) Hz, 2H), 3.60 (s, 6H), 2.69 (s, 4H), 2.08 (s, 3H), 2.08 – 1.98 (m, 2H), 1.10 (d, \(J = 4.7\) Hz, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.11, 162.35, 147.19, 142.87, 140.65, 138.06, 136.02, 131.46, 130.41, 129.31, 128.74, 128.58, 126.23, 124.88, 121.97, 110.49, 100.26, 48.57, 31.80, 27.74, 27.57, 24.72, 21.32, 18.90. HRMS (ESI\(^{+}\)) calcd 539.3421, found 539.3418 for C\(_{39}\)H\(_{43}\)N\(_2\)\(^{+}\) (M\(^+\)).

1,1,3-Trimethyl-2-(2-(2'-methyl-6-(2-(1,1,3-trimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-1H-benzo[e]indol-3-ium chloride [IR813-Ph(Me)]: Following General Procedure B, IR813=O (25 mg, 0.045 mmol) was reacted with 2-bromotulene (92 mg, 0.54 mmol) and n-BuLi (2.3 M, 0.16 mL, 0.36 mmol) to give IR813-Ph(Me) as a yellowish-green solid (20 mg, 67%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 – 7.83 (m, 6H), 7.62 – 7.36 (m, 9H), 7.20 (d, \(J = 14.1\) Hz, 2H), 7.11 (d, \(J = 7.5\) Hz, 1H), 6.10 (d, \(J = 14.1\) Hz, 2H), 3.72 (s, 6H), 2.73 (t, \(J = 6.6\) Hz, 4H), 2.15 (s, 3H), 2.12 – 2.02 (m, 2H), 1.42 (s, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 173.51, 161.67, 146.21, 140.25, 138.23, 136.07, 133.10, 131.80, 131.31, 130.70, 130.47, 130.19, 129.37, 128.73, 128.58, 126.23, 124.88, 121.97, 110.49, 100.26, 48.57, 32.12, 27.32, 21.39, 18.96. HRMS (ESI\(^{+}\)) calcd 639.3734, found 639.3698 for C\(_{47}\)H\(_{47}\)N\(_2\)\(^{+}\) (M\(^+\)).

2-(tert-Butyl)-4-(2-(6-(2-(tert-butyl)-7-(dimethylamino)-4H-chromen-4-ylidene)ethylidene)-2'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-7-(dimethylamino)chromenylium chloride [Chrom7-Ph(Me)]: Following General Procedure B, Chrom7=O (10 mg, 0.017 mmol) was reacted with 2-bromotulene (35 mg, 0.20 mmol) and n-BuLi (2.3 M, 0.06 mL, 0.14 mmol) to give Chrom7-Ph(Me) as a dark purple solid (7.6 mg, 63%). \(^1\)H NMR (400 MHz, MeOD) \(\delta\) 7.92 (d, \(J = 9.3\) Hz, 2H), 7.49 – 7.33 (m, 3H), 7.13 (d, \(J = 7.3\) Hz, 1H), 7.06 (d, \(J = 13.7\) Hz, 2H), 6.94 (dd, \(J = 9.3, 2.6\) Hz, 2H), 6.85 (d, \(J = 13.8\) Hz, 2H), 6.54 (d, \(J = 2.5\) Hz, 2H), 6.05 (s, 2H), 3.11 (s, 12H), 2.13 (s, 3H), 2.11 – 1.98 (m, 2H), 1.20 (s, 18H). \(^{13}\)C NMR (101 MHz, MeOD) \(\delta\) 169.35, 158.75, 156.31, 154.49, 145.27, 141.95, 137.98, 133.39, 130.51, 129.66, 127.93, 125.29, 125.18, 117.59,
112.75, 111.51, 109.74, 98.37, 96.89, 39.02, 36.01, 26.74, 24.94, 21.44, 18.14. HRMS (ESI\(^+\)) calcd 679.4258, found 679.4250 for C\(_{47}H_{55}N_{2}O_{2}\)\(^+\) (M\(^+\)).

![Chemical Structure](IR1061=O)

4-(2-(6-(2,6-diphenyl-4H-thiopyran-4-ylidene)ethyldiene)-2'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-2,6-diphenylthiopyrylium chloride [IR1061-Ph(Me)]: Following General Procedure B, IR1061=O (28 mg, 0.043 mmol) was reacted with 2-bromotulene (88 mg, 0.52 mmol) and \(n\)-BuLi (2.3 M, 0.15 mL, 0.35 mmol) to give IR1061-Ph(Me) as a dark purple solid (17 mg, 56%). \(^1\)H NMR (400 MHz, CDCl\(_3\) and MeOD) \(\delta 7.62\) – 7.39 (m, 20H), 7.39 – 7.28 (m, 7H), 7.14 – 7.02 (m, 3H), 6.66 (d, \(J = 14.0\) Hz, 2H), 2.88 (s, 6H), 2.83 – 2.64 (m, 4H), 2.07 – 1.90 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\) and MeOD) \(\delta 135.68, 131.46, 130.67, 130.16, 129.65, 128.23, 126.59, 125.60, 124.41, 123.02, 25.50, 21.37, 19.48. HRMS (ESI\(^+\)) calcd 717.2644, found 717.2683 for C\(_{51}H_{41}S_{2}\)\(^+\) (M+H\(^+\)).

General Procedure C: preparation of meso-substituted heptamethine dyes. Unless otherwise noted, aryl bromide (0.34 mmol) was dissolved in dry THF (1 mL) and cooled to -84 °C. To this solution was added \(t\)-BuLi (1.7 M in pentane, 0.40 mL, 0.68 mmol). The mixture was stirred for 40 min at this temperature. A red to orange solution of keto-heptamethine (0.042 mmol) in dry THF (1 mL) was added dropwise. The mixture was allowed to warm up to room temperature and stirred for 30 min. The yellow or orange reaction mixture was quenched by adding 1:10 HCl which resulted in a rapid color change into dark green. The mixture was diluted in H\(_2\)O and extracted with CH\(_2\)Cl\(_2\) (×4) and dried (Na\(_2\)SO\(_4\)). The crude product was purified by column chromatography (1:30 to 1:20 methanol / CH\(_2\)Cl\(_2\)).

![Chemical Structure](IR780=O)

2-(2-(6-(2,3,3-Dimethyl-1-propylindolin-2-ylidene)ethyldiene)-2',6'-dimethyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride [IR780-Ph(2Me)]: Following General Procedure C, IR780=O (22 mg, 0.042 mmol) was reacted with 2-bromo-1,3-dimethylbenzene (62 mg, 0.34 mmol) and \(t\)-BuLi (1.7 M, 0.40 mL, 0.68 mmol) to give IR780-Ph(2Me) as a green solid film (20 mg, 75%). \(^1\)H NMR (400 MHz, MeOD) \(\delta 7.42\) – 7.28 (m, 7H), 7.28 – 7.21 (m, 4H), 7.18 (t, \(J = 7.5\) Hz, 2H), 6.21 (d, \(J = 14.1\) Hz, 2H), 4.06 (t, \(J = 7.4\) Hz, 4H), 2.75 (s, 4H), 2.12 (s, 6H), 2.10 – 2.05 (m, 2H), 1.83 (h, \(J = 7.3\) Hz, 4H), 1.15 (s, 12H), 1.02 (t, \(J = 7.4\) Hz, 6H). \(^{13}\)C NMR (101 MHz, MeOD) \(\delta 173.46, 162.69, 146.98, 143.78, 142.22, 138.95, 137.16, 129.70, 129.50, 129.13, 125.92, 123.34, 111.86, 101.06, 49.93, 46.37, 28.19, 25.40, 22.60, 21.72, 19.42, 14.43, 11.65. HRMS (ESI\(^+\)) calcd 609.4203, found 609.4196 for C\(_{44}H_{53}N_{2}\)\(^+\) (M\(^+\)).
2-(2-((2',6'-Bis((allyloxy)methyl)-6-(2-(3,3-dimethyl-1-propylindolin-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride [IR780-Ph(2CH₂OAllyl)]: Following General Procedure C, IR780=O (22 mg, 0.042 mmol) was reacted with S2 (100 mg, 0.34 mmol) and t-BuLi (1.7 M, 0.40 mL, 0.68 mmol) to give IR780-Ph(2CH₂OAllyl) as a green solid film (29 mg, 91%).

\[
\begin{align*}
\text{IR780=O} & \quad \text{IR780-Ph(2CH₂OAllyl)}
\end{align*}
\]

Following General Procedure C, IR780=O (22 mg, 0.029 mmol) was reacted with p-toluenesulfinic acid (36 mg, 0.23 mmol) and Pd(PPh₃)₄ (6.7 mg, 0.0058 mmol) were dissolved in ethanol (2 mL) followed by three freeze-pump-thaw cycles. The mixture was stirred at 65°C under N₂ for 4.5 h. The reaction was diluted in CH₂Cl₂, washed with sat. NaHCO₃ and dried (Na₂SO₄). The crude product was purified by column chromatography (1:8 methanol / CH₂Cl₂) to give IR780-Ph(2CH₂OH) as a green solid film (13 mg, 66%).

\[
\begin{align*}
\text{IR780-Ph(2CH₂OAllyl)} & \quad \text{IR780-Ph(2CH₂OH)}
\end{align*}
\]

2-(2-(6-(2-(3,3-Dimethyl-1-propylindolin-2-ylidene)ethylidene)-2',6'-bis(hydroxymethyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-3,3-dimethyl-1-propyl-3H-indol-1-ium chloride [IR780-2C18]: Following General Procedure C, IR780=0 (22 mg, 0.042 mmol) was reacted with S3 (100 mg, 0.34 mmol) and t-BuLi (1.7 M, 0.40 mL, 0.68 mmol) to give IR780-2C18 as a green solid film (29 mg, 91%).
General Procedure C, t-BuLi (1.7 M, 0.40 mL, 0.68 mmol) was added to S3 (238 mg, 0.34 mmol) in THF solution and warmed up to room temperature until all solids were dissolved, at which point IR780=O (22 mg, 0.042 mmol) was added and stirred for 15 min. Subsequent work-up and column chromatography gave IR780-2C18 as a green solid (25 mg, 51%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.27 (m, 4H), 7.18 – 7.04 (m, 6H), 6.49 (s, 2H), 6.04 (d, $J = 14.1$ Hz, 2H), 4.00 (t, $J = 7.3$ Hz, 4H), 3.33 (t, $J = 7.3$ Hz, 4H), 2.66 (t, $J = 5.9$ Hz, 4H), 2.03 (p, $J = 5.3$ Hz, 2H), 1.98 (s, 6H), 1.84 (h, $J = 7.3$ Hz, 4H), 1.65 – 1.56 (m, 4H), 1.28 (d, $J = 69.3$ Hz, 64H), 1.16 (s, 12H), 1.02 (t, $J = 7.4$ Hz, 6H), 0.84 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.79, 164.06, 146.57, 142.80, 141.04, 136.54, 131.76, 128.78, 124.66, 121.98, 112.47, 110.73, 100.22, 51.46, 48.79, 46.18, 32.00, 29.90 – 29.72 (m), 29.40, 28.01, 27.55, 27.38, 24.87, 22.72, 21.60, 20.88, 19.97, 14.05, 11.65. HRMS (ESI$^+$) calcd 1128.9946, found 1128.9935 for C$_{80}$H$_{126}$N$_3$+$^+$ (M$^+$).
NMR Spectra
References


