Supporting materials for:

Amphiphilic Block Copolymer Conjugated with Carborane and NIR Fluorescent Probe for Potential Imaging-guided BNCT Therapy

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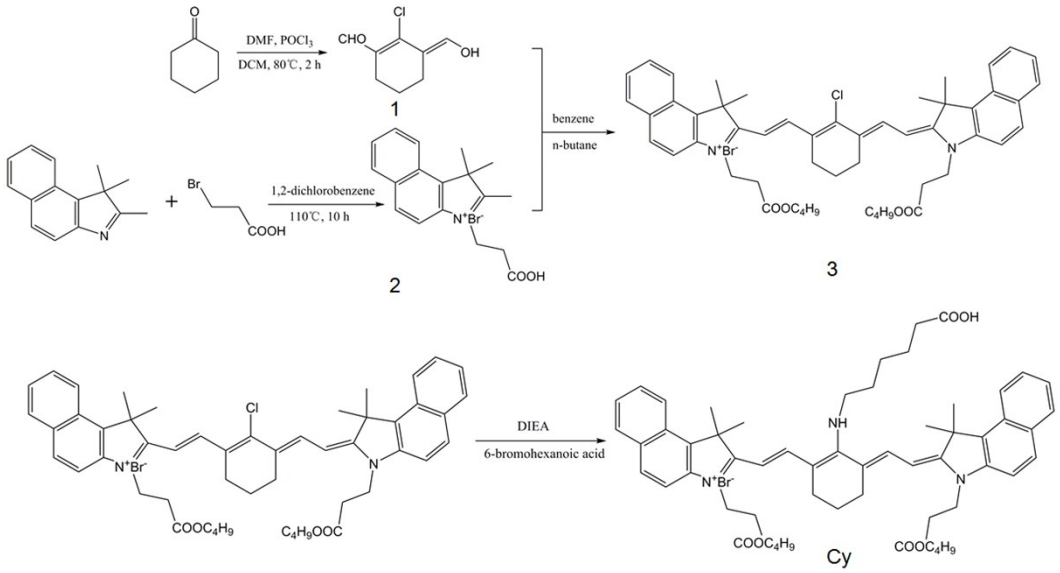
The synthesis of Cyanine dye:



Scheme S1. The synthesis route of the NIR aminocyanine (Cy) dye we used.

This Cyanine dye was prepared in 68 % yield according to a literature Method.[1] In brief, 1-hydroxycarbonylethyl-2,3,3-trimethylbenzoindoleninium bromide (0.42g, 1.16mmol) and 2-chloro-1-formyl-3-(hydroxymethylene)cyclohex-1-ene (0.10g, 0.58mmol) were dissolved into a mixed solvent of benzene (15 mL) andn-butanol (35 mL) in a two-necked flask fitted with a Dean–Stark trap and a condenser. The mixture was heated to 110 °C under a nitrogen atmosphere for 16 h, after which the solvent was removed under vacuum. The obtained green solid was washed with ether and purified by

normal phase column chromatography, with a gradient elution from EtOAc to EtOAc/methanol (5:1). Removing the solvent after column chromatography yields 0.35 g dye (68% yield) as a deep green solid.

Then the green solid we obtained (150mg, 0.17mmol) and 6-aminocaproic acid (30 mg, 0.23mmol) were added to 5 mL dry DMF, followed by the addition of 29mL DIEA (22mg, 0.17mmol). The obtained solution was heated to 70°C and stirred in the dark for 8 h. The solvent was then removed under vacuum, and the obtained deep blue solid was washed with ether and further purified by a column chromatography method with gradient elution from EtOAc to EtOAc/methanol (5:1). 100mg (59% yield) deep blue solid was obtained after removing the solvent under vacuum. The ^{1}H NMR of intermediate products 1, 2, 3 and final Cy were shown below.

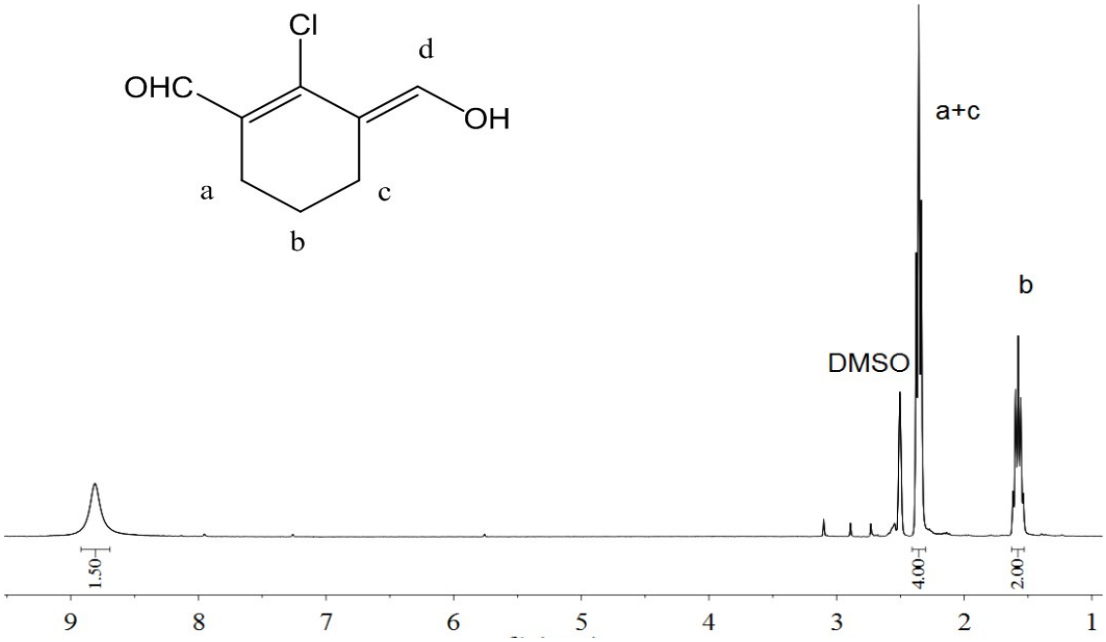


Figure S1. ^{1}H NMR of 2-chloro-1-formyl-3-(hydroxymethylene)cyclohex- 1-ene(Compound 1).

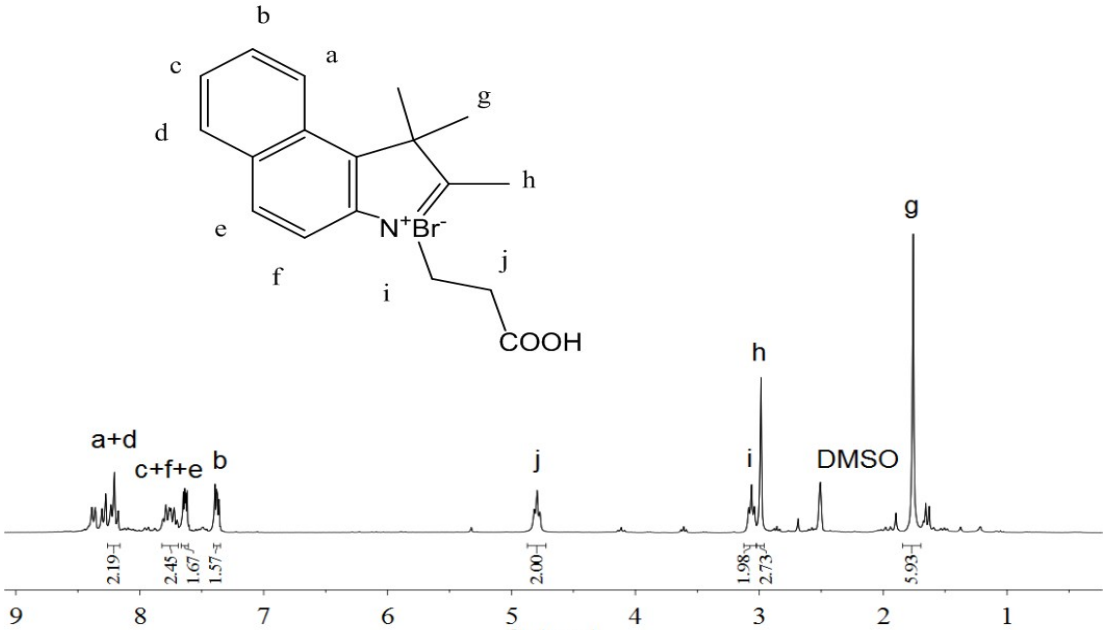


Figure S2. ^{1}H NMR of intermediate product 2.

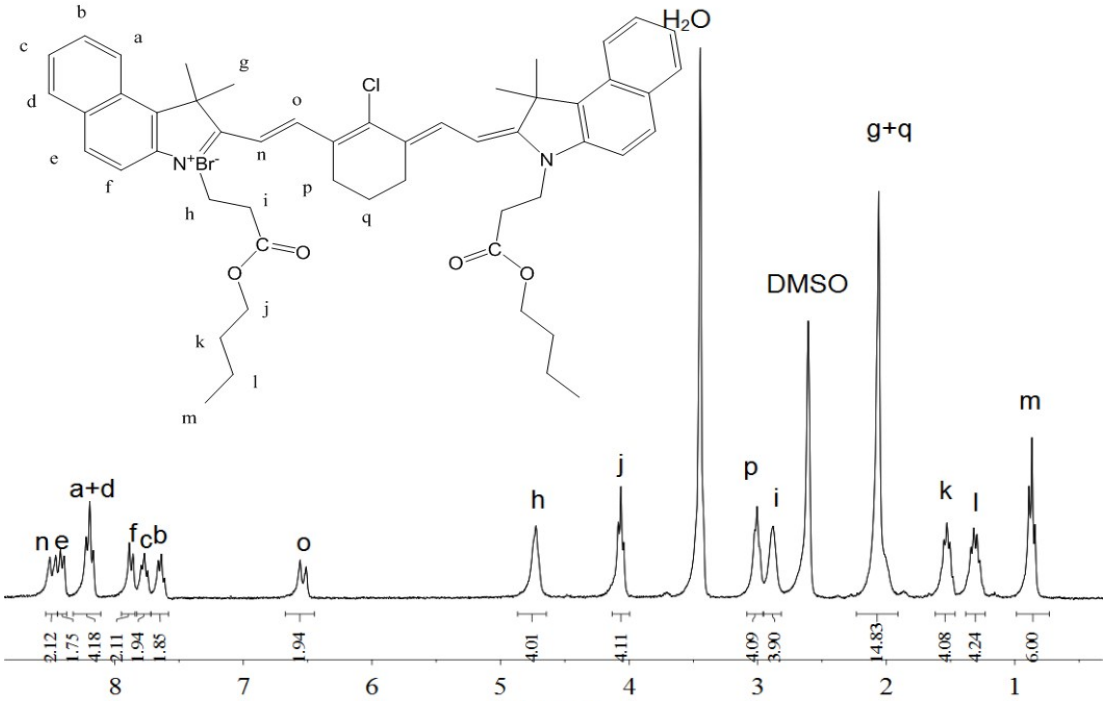


Figure S3. ^{1}H NMR of intermediate product 3.

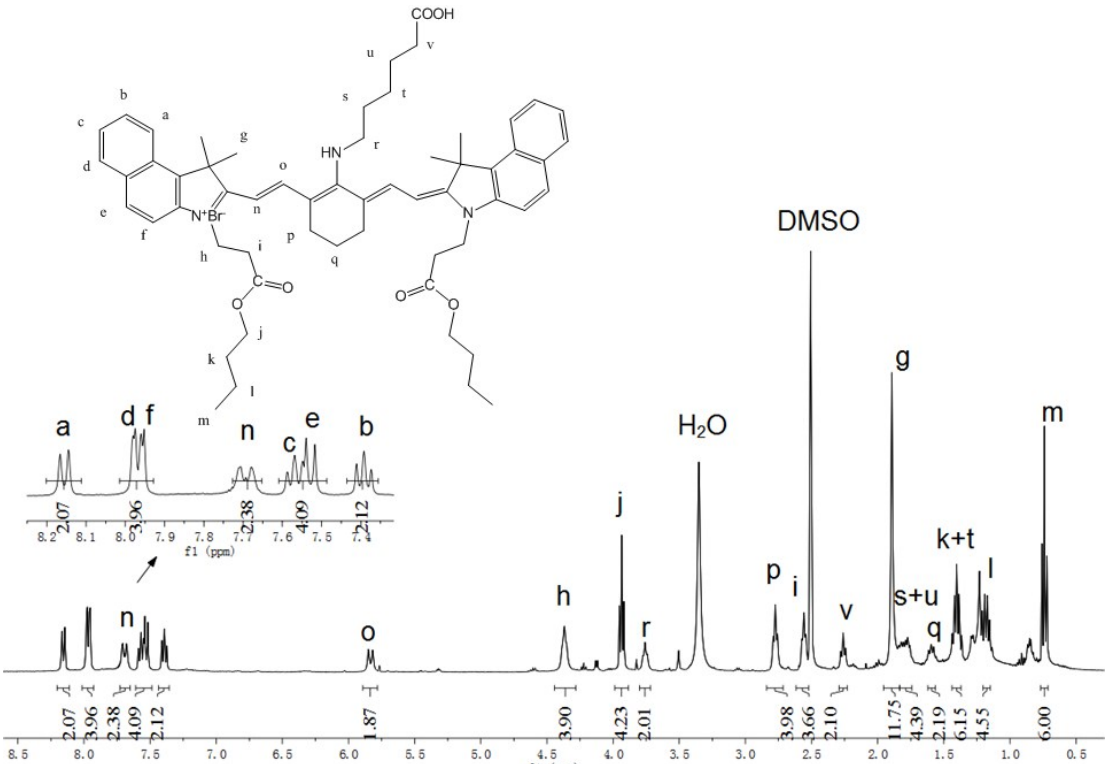


Figure S4. ^{1}H NMR of the final Cy dye we used.

[1]. Zhang ZR, Achilefu S. Synthesis and evaluation of polyhydroxylated near-infrared carbocyanine molecular probes. Org Lett. 2004,6(12):2067-70.