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Metal ion induced FRET On–Off in naphthyl-pyrenyl pendent tetrahomodioxacalix[4]arene

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ABSTRACT

A novel tetrahomodioxacalix[4]arene (**7**) bearing both naphthyl- and pyrenyl-amide pendants was synthesized as FRET-based fluorometric sensor for Cu^{2+} ion. Intramolecular FRET from the naphthalene emission to the pyrene absorption affords Cu^{2+} ion selectivity over other metal ions. Upon addition of Cu^{2+} ion, the complex solution of **7** gave a significantly decreased pyrene acceptor emission along with an enhancement of naphthalene donor emission *via* FRET On–Off event.

Many heavy and transition metal ions, such as Hg^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+}, have received considerable attention because of its widespread use in agricultural, chemical and industrial processes, which are becoming threats to living organisms.[1] In particular, Cu(II) is an essential element playing a fundamental role in the biochemistry of the human nervous system, but is toxic with high concentration.[2] Thus, its accumulation in the human body affects an oxidative stress and disorders associated with neurodegenerative diseases, Menkes disease, Wilson disease, and Alzheimer's disease.[3] Therefore, development of the chemosensors specifically for the Cu^{2+} has been greatly interesting in many fields.[4]

Many chemosensors were prepared by attachment of fluorophore units to macrocyclic or chelating molecules. Among the macrocyclic frameworks, a class of calix[4]arene is a good candidate for the chemosensor framework towards specific metal ion because of their characteristic cavity size or geometrically restricted conformation.[5] However, homooxacalix[4]arenes, having extra oxygen atoms in the macrocyclic ring, have received little attention because they can only be synthesized in relatively low yields.[6–8] Tetrahomodioxa *p*-*tert*-butylcalix[4]arene was prepared by Gutsche in 44% yield by dehydration of a bishydroxymethylated dimer of *p*-*tert*-butylphenol, which was synthesized by a multistep reaction starting from the bromination of *p*-*tert*-butylphenol.[8] There have only been limited studies on the solution conformations, solid-state structures, and on complexation behavior of homooxacalix[4]arenes.[9–12] We also previously reported that there are five conformations in tetrahomodioxacalix[4]arene with appropriate nomenclature (cone, partial cone, C-1,2-alternate, COC-1,2 alternate, and 1,3-alternate) as represented in Figure 1.[13] Recently, we also reported a solid-state structure of C-1,2-alternate *N*,*N*-diethyl tetrahomodioxacalix[4]arene tetraamide complexing

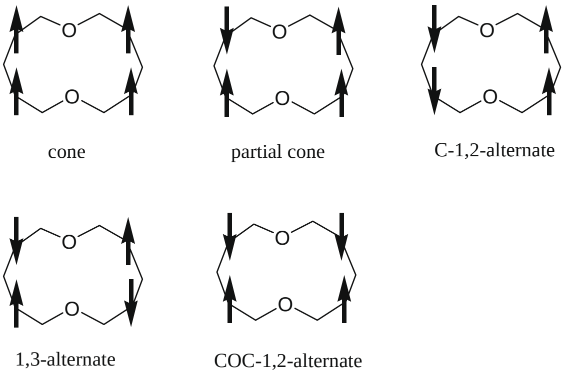
cone
partial cone
C-1,2-alternate
1,3-alternate
COC-1,2-alternate

Figure 1. Schematic representation of the five conformations of homooxacalix[4]arenes.

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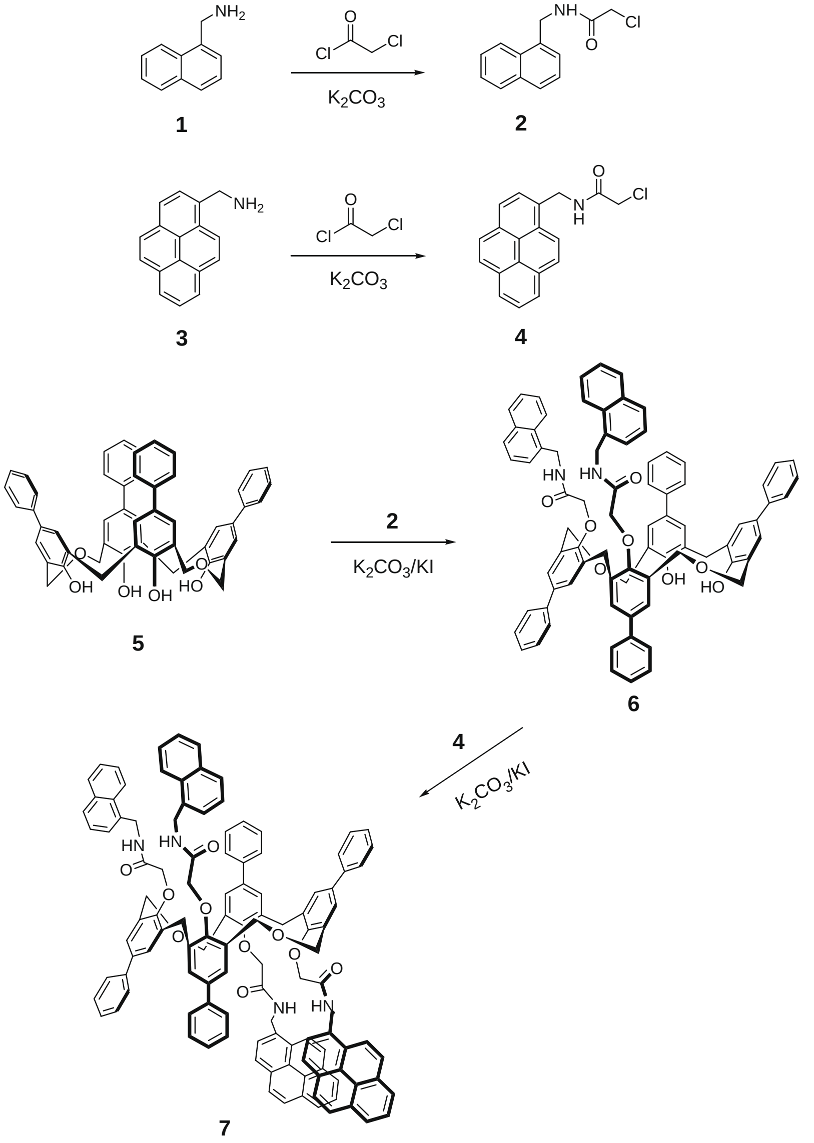
Pb^{2+} proven by X-ray structure.[14] For a corresponding *mono*alkyl amide, the conformation changed to 1,3-alternate due to intramolecular hydrogen bonding, resulting in weak binding of metal ions.[14]

We also previously reported that a series of C-1,2-alternate tetrahomodioxacalix[4]arene pyreneamides were synthesized. Pb^{2+} coordination gave a quenched monomer and excimer fluorescence emission, while upon Ca^{2+} ion binding the receptor provides an enhanced excimer and declined monomer emission with ratiometric response. Upon Ca^{2+} binding, the efficient HOMO–LUMO interaction between Py and Py^* induces a formation of strong excimer emission band, whereas there is no such interaction observed upon Pb^{2+} complexation.[15,16]

Fluorescence chemosensors utilize photophysical changes produced by cation binding: photo-induced electron transfer (PET);[17] photo-induced charge transfer (PCT);[18] excimer/exciplex formation and extinction;[19] or fluorescence resonance energy transfer (FRET).[20] The FRET is known to be sensitive, selective, and adaptable to a wide variety of systems.[21] However, reports on FRET-based metal ion sensors are still at a modest number. The FRET arises from a donor–acceptor (D–A) interaction between a pair of fluorophores in their excited state. Excited state of the fluorescent donor is then non-radiatively transferred to the acceptor, and the donor returns to its electronic ground state. Therefore, the FRET is required to have a certain extent of spectral overlap between emission spectrum of the donor and absorption spectrum of the acceptor.[22] From this point of view, we herein report on synthesis and the fluorescence properties of tetrahomodioxacalix[4]arene bearing naphthyl- and pyrenyl-amides (**7**) able to show the FRET On→Off by the Cu^{2+} ion.

The synthetic routes[23] for tetrahomodioxacalix[4]arene derivatives **6** and **7** are described in Scheme 1. Synthesis of **6** was performed by the condensation of *N*-(1-naphthalenemethyl) chloroacetamide (**2**) with tetrahomodioxacalix[4]arene (**5**)[24] in the presence of K_2CO_3 as a base and a catalytic amount of KI. Reaction of **6** with *N*-(1-pyrenylmethyl)chloroacetamide (**4**)[25] under basic medium gave **7** in 72% yield.

There are two different shapes in 1,2-alternate conformations on tetrahomooxacalixarene system. 1,2-alternate conformer in which the adjacent *syn* aryl moieties are joined by a CH_2 group is designated as the C-1,2-alternate, while the 1,2-alternate conformer in which the adjacent *syn* aryl moieties are joined by a $CH_2–O–CH_2$ moiety is designated as the COC-1,2-alternate.[14] The dimethylenoxy protons of the ArCH_2OCH_2Ar bridge showed AB



Scheme 1. Synthetic pathways to **6** and **7**.

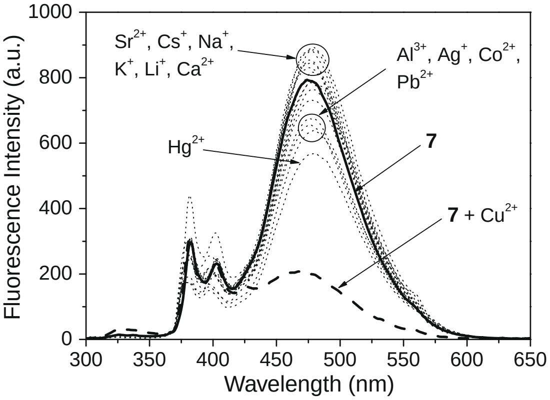


Figure 2. Fluorescence spectra of **7** (6.0 μM) upon addition of various cations (100.0 equiv) in $CH_3CN/CHCl_3$ (40:1, v/v) with an excitation wavelength at 280 nm.

doublets at δ 4.86 and δ 4.07 ($\Delta v = 316$ Hz) with a *geminal* coupling constant of 13.0 Hz. A doublet with peaks for the methylene protons of ArCH_2Ar showed at δ 3.75 and δ 3.04 ($\Delta v = 284$ Hz) with a *geminal* coupling constant of 11.4 Hz. The ^{13}C NMR spectrum showed one peak at 62.38 ppm for the $ArCH_2O$ bridge methylenoxy carbons and one peak at 30.36 ppm for the ArCH_2Ar bridge carbons also indicating that two adjacent benzene rings are in a *syn* orientation (C-1,2-alternate conformation).

For the detailed study of FRET occurring in **7**, we examined its fluorescence and UV/vis spectral behaviors upon addition of various metal ions such as Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cu^{2+}, Co^{2+}, Ba^{2+}, Pb^{2+}, Ca^{2+}, Hg^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, and Al^{3+}. As seen in Figure 2, **7** shows a weak naphthalene emission at 331 nm and strong pyrene monomer and excimer emission bands at 382 and 470 nm, respectively, with an excitation at 280 nm. Interestingly, we observed increase in naphthalene emission shown at 331 nm along with decreased pyrene excimer emission at 470 nm upon addition of Cu^{2+} ion. We envisioned that these fluorescence changes may associate with the FRET changes upon Cu^{2+} binding. In the solution of **7**, FRET-On occurs by overlapping of naphthalene emission (donor fluorophore) with pyrene absorption (acceptor fluorophore) as seen in Figure 3a. Thus, **7** exhibits a weak naphthalene emission and strong pyrene emission bands although the excitation wavelength is 280 nm which corresponds to the naphthalene absorption band.

Upon addition of Cu^{2+} ion to a solution of **7**, however, we noticed that the naphthalene emission band at 331 nm increases, but the pyrene emission concomitantly declines. This is attributable to the fact that the pyrene absorption band of **7** decreases upon addition of Cu^{2+} ion (Fig. 3b), then the spectral overlap between naphthalene and pyrene is minimized to give the decline in FRET efficiency. With respect to the extent of FRET changes, **7** indicates a high selectivity toward Cu^{2+} ion over other metal cations.

To gain insight into the FRET efficiency in the energy transfer process from naphthalene to pyrene, the photophysical property of **6** in the absence of the pyrene units as an energy acceptor was also studied. The FRET efficiency can be estimated by the following equation:[26]

$$E = 1 - (F'_D/F_D)$$

where E denotes FRET efficiency; F'_D and F_D are the donor fluorescence intensity with and without an acceptor, respectively. As seen in Figure 4, **7** without copper ion barely exhibits naphthalene emission band at 331 nm because of FRET occurring. However, addition of Cu^{2+} ion to a solution of **7** increases the naphthalene emission intensity due to the FRET-Off (inset). From the fluorescence changes, E of **7** and **7**·Cu^{2+} was calculated to be 0.58 and 0, respectively.

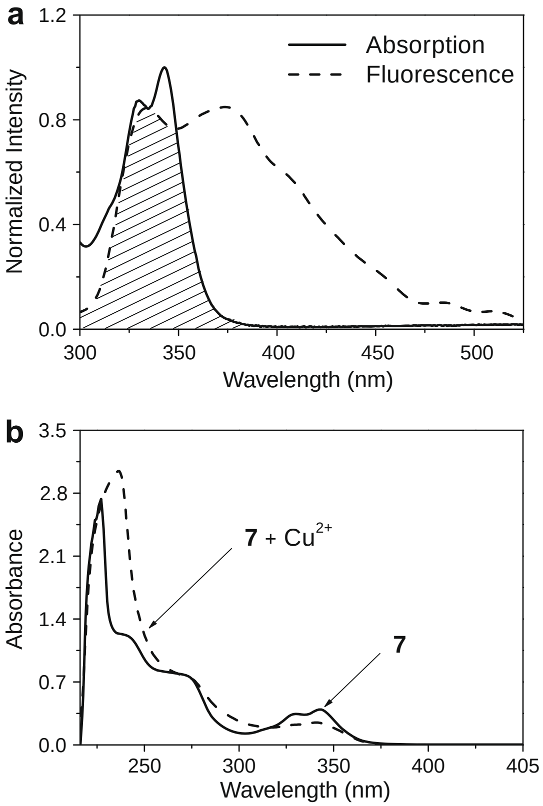


Figure 3. (a) Spectral overlap of naphthalene emission (FRET donor) and pyrene absorption (FRET acceptor). (b) Absorption spectral changes of **7** in the absence and in the presence of Cu^{2+} ion (100.0 equiv).

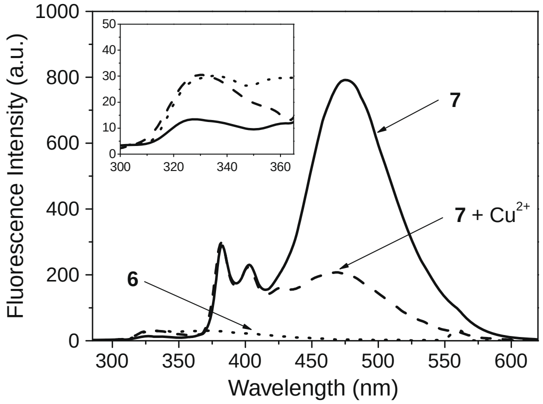


Figure 4. Fluorescence spectra of **6** and **7** (6.0 μM, respectively) in the presence of Cu^{2+} ion (100.0 equiv) in $CH_3CN/CHCl_3$ (40:1, v/v) with an excitation at 280 nm. Inset: enlarged spectra of **6** and **7** between 300 and 365 nm.

Moreover, we observed a selective visual fluorescence change of **7** upon addition of Cu^{2+} ion over other various metal ions, which is obviously due to the FRET-Off to give a decreased pyrene emission of **7** (Fig. 5).

Figure 5. Visual fluorescence changes of **7** (10.0 μM) upon addition of various metal ions in $CH_3CN/CHCl_3$ (40:1, v/v). From left to right: free **7**, Cu^{2+}, K^+, Li^+, Na^+, Cs^+, Rb^+, Ag^+, Co^{2+}, Ba^{2+}, Pb^{2+}, Ca^{2+}, Hg^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, and Al^{3+} (100.0 equiv, respectively).

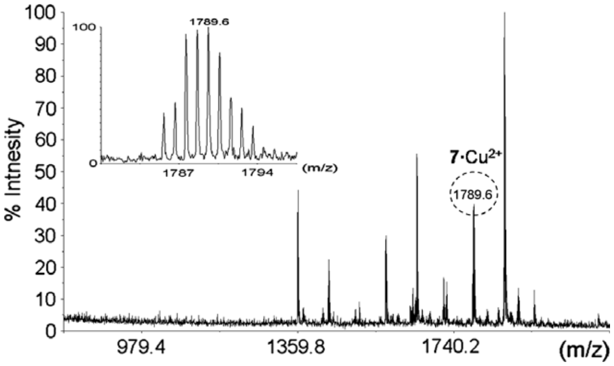


Figure 6. MALDI–TOF Mass spectrum of **7**·Cu^{2+}.

For the binding mode between **7** and Cu^{2+} ion, MALDI-TOF Mass analysis was carried out. A peak at 1789.6 *m/z* corresponding to **7**·Cu^{2+} was observed by addition of excess Cu(ClO$_4$)$_2$ to **7** as seen in (Fig. 6). We then noticed that the Cu^{2+} ion is coordinated by **7** with an 1:1 stoichiometry.

In conclusion, FRET-based fluorometric tetrahomodioxacalix[4]arene **7** has been newly synthesized. Derivative **7** exhibits a weak naphthalene emission and a strong pyrene emission to provide a FRET-On due to an energy transfer event from naphthalene to pyrene unit. Complexation with Cu^{2+} increases the naphthalene emission along with decreases in the excimer emission of **7** because of the FRET-Off. With respect to the extent of FRET changes, we could observe the Cu^{2+} selectivity of **7** over other metal ions.

Acknowledgments

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23. Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Melting points were taken in evacuated and sealed capillary tubes with a Mel-Temp apparatus and were uncorrected. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX 400 spectrometer. Chemical shifts are recorded in parts per million relative to TMS as an internal standard.
    N-(1-naphthalenemethyl)chloroacetamide (**2**). To a suspension of 1-naphthalenemethylamine (300 mg, 1.91 mmol) and potassium carbonate (1.10 g, 7.64 mmol) in a mixture of water (50 mL) and ethyl acetate (50 mL), a solution of chloroacetyl chloride (0.25 mL, 3.14 mmol) in ethyl acetate (10 mL) was added dropwise. After the reaction mixture was stirred at room temperature for 2 h, organic phase was separated and dried over anhydrous magnesium sulfate. The residue obtained by evaporation of solvent was triturated with hexane to afford 440 mg (98%) as a colorless crystalline solid. mp 120 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00–7.44 (m, 7, Ar*H*), 6,82 (br. s, 1, N*H*), 4.95 (d, 2, CH$_2$, J = 5.6 Hz), 4.11 (s, 2, CH$_2$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.79 (*C*=O), 134.10, 132.73, 131.52, 129.17, 129.11, 127.06, 126.98, 126.34, 125.61, 123.40 (Ar), 42.80, 42.20 (*C*H$_2$). Anal. Calcd for $C_{13}H_{12}NOCl$: C, 66.81; H, 5.18. Found. C, 66.89; H, 5.17.
    7,13,21,27-Tetraphenyl-29,31-bis[(N-(1-naphthalenylmethyl)aminocarbonyl)-methoxy]-30,32-dihydroxy-2,4,16,18-tetraho-mo-3,17-dioxacalix[4]arene (**6**). Tetrahomodioxacalix[4]arene **5** (571 mg, 0.724 mmol), potassium carbonate (100 mg, 0.726 mmol), potassium iodide (50 mg), and **2** (400 mg, 1.81 mmol) in dried acetone (100 mL) was refluxed 80 h. After evaporation of solvent, the residue was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and evaporated in vacuo. The residue was triturated with MeOH to give the product mixture which was recrystallized from methanol to afford 676 mg (80%) of the desired product as a pale yellow colored crystal. Mp 140–141 °C (decomposed); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (d. 1, Ar*H*, J = 6.6 Hz), 8.14 (d. 1, Ar*H*, J = 6.6 Hz), 8.04 (d, 2, Ar*H*, J = 8.8 Hz), 7.65–7.03 (m, 38, Ar*H*, N*H* and O*H*), 6.90 (d, 4, Ar*H*, J = 9.2 Hz), 5.29 (d, 1, NC*H*$_2$Nap, J = 14.4 Hz), 5.28 (d, 1, NC*H*$_2$Nap, J = 14.4 Hz), 4.75 (d, 1, NC*H*$_2$Nap, J = 14.4 Hz), 4.74 (d, 1, NC*H*$_2$Nap, J = 14.4 Hz), 4.62 (s, 4, OC*H*$_2$CO), 4.61 (d, 2, ArC*H*$_2$O, J = 14.8 Hz), 4.51 (d, 2, ArC*H*$_2$O, J = 14.8 Hz), 4.39 (d, 2, ArC*H*$_2$O, J = 10.4 Hz), 4.26 (d, 2, ArC*H*$_2$O, J = 10.4 Hz), 3.87 (d, 2, ArC*H*$_2$Ar, J = 14.0 Hz), 2.96 (d, 2, ArC*H*$_2$Ar, J = 14.0 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 168.24 (*C*=O), 153.60, 153.41, 141.14, 140.25, 138.17, 134.36, 133.86, 133.03, 132.57, 131.51, 130.47, 130.07, 129.44, 129.07, 129.01, 128.83, 128.76, 128.21, 127.83, 127.37, 127.18, 127.13, 127.03, 126.93, 126.56, 125.84, 125.49, 125.25, 123.54, 122.56 (Ar), 73.32 (OCH$_2$CO), 73.04, 71.02 (ArCH$_2$O), 41.71 (NCH$_2$Np), 28.88 (ArCH$_2$Ar). Anal. Calcd for $C_{80}H_{66}O_8N_2$: C, 81.20; H, 5.62. Found. C, 81.91; H, 5.66.
    7,13,21,27-Tetraphenyl-29,31-bis[(N-(1-naphthalenylmethyl)amino-carbonyl)-methoxy]-30,32-bis[N-(1-pyrenylmethyl)aminocarbonyl]-methoxy]-2,4,16,18-tetrahomo-3,17-dioxacalix[4]arene (**7**). A mixture of **6** (421 mg, 0.316 mmol), potassium carbonate (262 mg, 1.90 mmol), **4** (419 mg, 1.79 mmol) and a trace catalytic amount of KI in dried CH_3CN (120 mL) was refluxed for 120 h. The solvent was evaporated and the residue was extracted with CH_2Cl_2. The organic layer was washed two times with water, dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue was triturated with hexane to give the product mixture which was recrystallized from methylene chloride and methanol to afford the pure product (393 mg, 72%) as a pale yellow colored crystal. Mp 113–114 °C (decomposed); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96–7.74 (m, 20, Ar*H* and N*H*), 7.62–7.34 (m, 36, Ar*H*), 7.19–6.62 (m, 8, Ar*H*), 5.12 (d, 2, NC*H*$_2$Ar, J = 12.0 Hz), 4.96 (d, 2, NC*H*$_2$Ar, J = 12.0 Hz), 4.86 (d, 2, ArC*H*$_2$O, J = 13.0 Hz), 4.83 (d, 4, OC*H*$_2$CO, J = 10.8 Hz), 4.61 (d, 2, NC*H*$_2$Ar, J = 11.2. Hz), 4.07 (d, 2, ArC*H*$_2$O, J = 13.0 Hz), 3.96 (d, 4, OC*H*$_2$CO, J = 10.8 Hz), 3.75 (d, 2, ArC*H*$_2$Ar, J = 12.4 Hz), 3.66 (d, 2, NC*H*$_2$Ar, J = 11.2. Hz), 3.04 (d, 2, ArC*H*$_2$Ar, J = 12.4 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 168.18 (*C*=O), 153.70, 139.44, 134.05, 133.08, 131.45, 131.16, 129.69, 129.0–129. 7, 129.00, 128.87, 127.99, 126.96, 126.90, 126.30, 126.21, 125.58, 125.37, 123.59, 123.40 (Ar), 71.26 (OCH$_2$CO), 62.38 (ArCH$_2$O), 41.28 (NCH$_2$Np), 30.36 (ArCH$_2$Ar). Anal. Calcd for $C_{118}H_{92}O_{10}N_4$: C, 82.11; H, 5.37. Found. C, 81.29; H, 5.36.
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