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Luminescence behaviour of calix[4]arenes bearing an increasing number of appended-pyrenes

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Abstract—Pyrene-appended calix[4]arenes **6**–**8** bearing an increasing number (from 2 to 4) of 'pyrene amide' residues have been prepared. Their fluorescence behaviour has been investigated to show dependence on the number of pyrene groups. Their behaviour as fluorophores is also described.

The increasing need for molecular sensors has stimulated intensive research in the design of molecular devices able to signal a specific substrate.[1] Fluorescent sensors offer several distinct advantages such as sensitivity, selectivity, time response and spatial resolution.[1] They consist of a fluorophore linked to a selective ionophore and is thus called fluoroionophore. Photo-physical sensing processes are diverse: photo-induced electron transfer (PET), photo-induced charge transfer (PCT), energy transfer and excimer formation.[1] Due to their well-known ionophoric properties, calixarenes[2] have been used to create fluoroionophores as luminescent molecular probes.[2a] Calix[4]arenes have been functionalized at the phenolic OHs by esters, ketones, carboxylic acids, amides, etc. to reach high recognition levels.[2] Amide group is known to complex cations through interactions with carbonyl oxygen atoms and anions through hydrogen bonding with –CON*H*– acidic hydrogens.[2] *N*-(1-Pyrenylmethyl) amide or 'pyrene-amide' is a useful fluorophore because it displays well-defined monomer emission at 370–430 nm and efficient excimer emission at around 480 nm.[3,4] The intensity ratio of excimer to monomer emission (I_E/I_M) is sensitive to conformational changes of the receptors on which they are attached and the variation of I_E/I_M values upon metal-ion binding is an informative parameter in sensing systems.[5–7] Two pyrene-amide groups form a strong intramolecular excimer through strong face-to-face π-stacking interaction.[8]

As a continuation of our work on luminescent pyrene amide calix[4]arenes[9] we have prepared pyrene-appended calix[4]arenes **6**–**8** (Chart 1) bearing an increasing number (from 2 to 4) of 'pyrene amide' residues. Their fluorescence behaviour has been investigated to show dependence on the number of pyrene groups and to develop new fluoroionophores based on calixarenes.[2a]

Compound **6** was prepared by reacting **1**[10] with 3 equiv of ethyl bromoacetate in the presence of 2 equiv of K_2CO_3 in refluxing CH_3CN for 24 h. Pure **6** was isolated after column chromatography on SiO_2 using AcOEt–hexane (3/1) as eluent.[11] The addition of two –CH_2CO_2Et groups on **1** was confirmed by the FAB-MS spectrum and microanalysis of **6**. The symmetrical disposition of the *O*-alkylating groups and the cone conformation were deduced from its ^{1}H NMR spectrum. Singlets at 4.47 ppm and 4.44 ppm were observed for ArOCH_2CONH– and ArOCH_2CO$_2$Et, respectively, while characteristic AB system of the cone conformation was found at 4.54 and 3.30 ppm with $J = 12.8$ Hz for the ArCH_2Ar of the calix[4] unit. A peak at 31.9 ppm in ^{13}C NMR spectrum also provided concrete evidence for the cone conformation. In a general manner, **2**–**8** were fully

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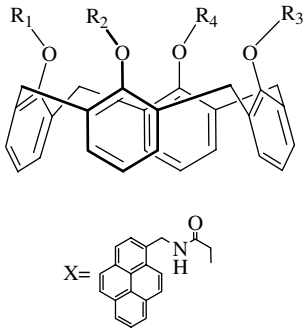

1 R_1=R_3=H, R_2=R_4=X
2 R_1=CH_2CO_2Et, R_2=R_3=R_4=H
3 R_1=R_2=R_3=R_4=CH_2CO_2Et
4 R_1=R_2=R_3=R_4=CH_2CO_2H
5 R_1=R_2=R_3=R_4=CH_2COCl
6 R_1=R_3=CH_2CO_2Et, R_2=R_4=X
7 R_1=CH_2CO_2Et, R_2=R_3=R_4=X
8 R_1=R_2=R_3=R_4=X

Chart 1. Cone calixarene derivatives **1**–**8**.

characterized by ^{1}H NMR, ^{13}C NMR, FAB-MS and elemental analysis.[11]

The synthesis of **7** begins by reacting calix[4]arene with 1 equiv of ethyl bromoacetate in the presence of 1 equiv of K_2CO_3 in refluxing CH_3CN for 24 h. Recrystallization of the crude mixture from Et_2O gave pure **2**, which was further reacted with 3 equiv of *N*-(1-pyrenylmethyl)chloroacetamide[9] in the presence of 5 equiv of K_2CO_3 in refluxing CH_3CN for 24 h to afford **7** pure after chromatography on SiO_2 with AcOEt–hexane (3/1) as eluent. Analytical data of **2** and **7** were in agreement with a cone conformation.[11] The synthesis of **8** begins by reacting calix[4]arene with 5 equiv of ethyl bromoacetate in the presence of 3 equiv of K_2CO_3 in refluxing CH_3CN for 12 h. Recrystallization of the crude mixture from Et_2O–MeOH (10/1) afforded **3**, which was hydrolyzed into **4** with 5 equiv of NaOH in refluxing H_2O–EtOH–THF (5/5/2) for 12 h. Treatment of **4** with an excess of $SOCl_2$ in dry toluene afforded acyl chloride **5**, which was directly reacted with 4 equiv of 1-pyrenemethylamine hydrochloride in the presence of 10 equiv of NEt_3 in refluxing THF for 2 days. Pure **8** was obtained by recrystallization from Et_2O. Both **3** and **8** were observed to be in the cone conformation. The ^{13}C-δ shifts of **2**–**8** are given in bold in the experimental section to show the cone conformation in agreement with the Mendoza rule.[11] Single crystals of **7** suitable for X-ray were obtained by slow evaporation of MeOH solution. The X-ray crystal structure confirmed the cone conformation of **7** as shown in Figure 1.[12]

The fluorescence emission spectra of **6**–**8** in $CHCl_3$–CH_3CN (1/3) (6.0 μM, λ_{ex} = 343 nm) are shown in Figure 2. The ratio of excimeric to monomeric emission of the pyrene moieties showed that the more pyrene units, the greater intensity in the excimer emission at λ_{em} = 472 nm is observed. By contrast, the intensity of the monomeric emission declines going from **6** to **8**. The ratio of excimer to monomer fluorescence intensity of **8** is about 5 times and 2 times greater than **6** and **7**, respectively. This is presumably because **8** forms more stable π–π stacking interactions between two facing pyrenes than **6** and **7**. The steering of the pyrene units by the rigid cone conformation of the calix[4] moiety may be argued to explain this behaviour. Metal ion binding properties of **6**–**8** were investigated by monitoring the

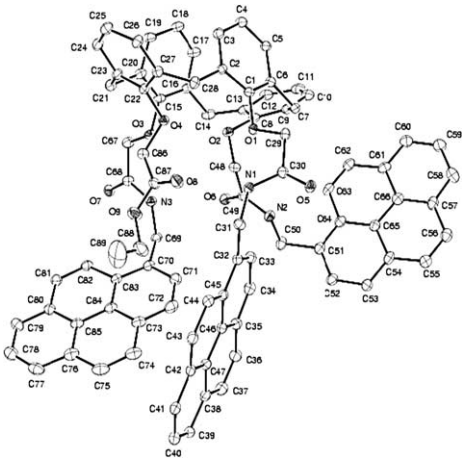

Figure 1. Solid state structure of **7**.

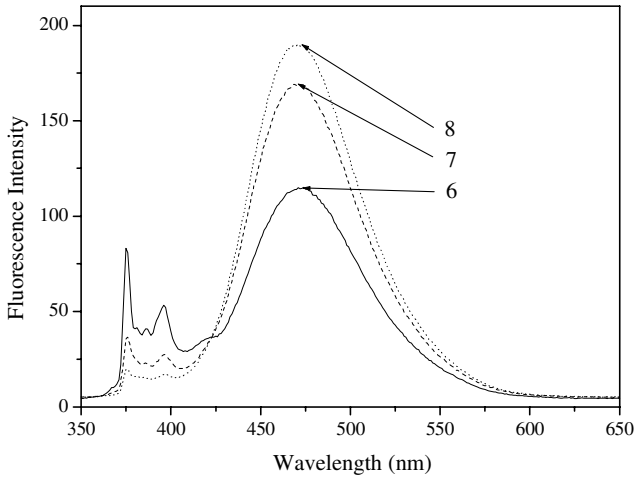

Figure 2. Fluorescence emission spectra of **6**–**8** (6.0 μM, excitation at 343 nm with 1.5 nm slit widths) in $CHCl_3$–CH_3CN (1/3).

fluorescence changes upon the addition of Li^+, Na^+, K^+, Zn^{2+}, Co^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Cu^{2+} and Pb^{2+}. Spectra for **6** are seen in Figure 3 in which the fluorescence changes are extremely diverse. Jin et al.[13] and Shinkai and co-workers.[14] previously found similar behaviour with related fluorogenic calix[4]arenes bearing two 1,3-opposite pyrene attached via ester linkages. We also observed a pronounced blue shift along with an intensity decrease of the pyrene excimer emission in the presence of Cu^{2+} (from 474 to 444 nm). Such a blue-shift is probably due to a locally excited and partially overlapped pyrene dimer with a rapid structural relaxation to the lower energy excimer.[15] No substantial emission changes were observed for **7** and **8** except for Pb^{2+} and Cu^{2+}. The Pb^{2+} probably quenched the fluorescence of **7** and **8** both in the excimer and in the monomer by a heavy metal ion effect[8a,9b,16] and/or a reverse-PET[17] from pyrene units due to complexation to carbonyl groups. Pyrene–Cu^{2+} complexes involve extensive charge transfer from Cu^{2+} d-orbitals to pyrene π*-orbitals[18] leading to a complete quenching. This heavy metal effect does not exist for the other metal ions.

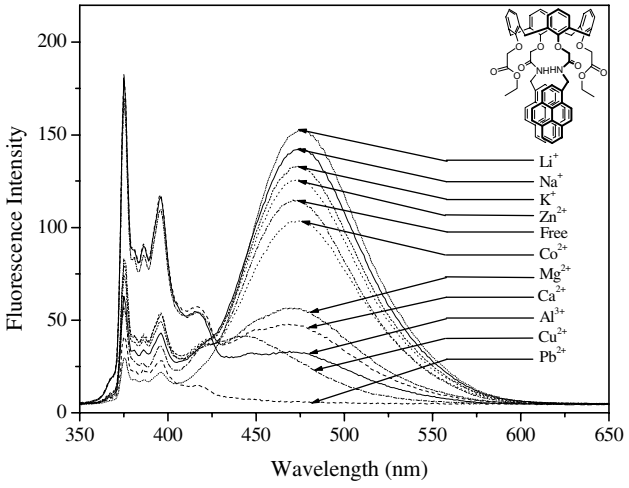

Figure 3. Fluorescence emission spectra of **6** (6.0 μM, excitation at 343 nm with 1.5 nm slit widths) upon the addition of various cations (0.01 M, 500 equiv) in $CHCl_3/CH_3CN$ (1/3).

In conclusion, we reported the synthesis of three new luminescent calix[4]arenes **6**–**8** bearing an increasing number of *N*-(1-pyrenylmethyl)acetamide functions. The ratio of excimeric to monomeric emission of the pyrene moieties was strongly dependent on the number of pyrene units attached to the calix unit. Complexation studies showed that **6** exhibited an interesting diversity in fluorescence changes depending upon the added cation. Compounds **7** and **8** were only sensitive to Pb^{2+} and Cu^{2+}.

Future work is directed towards: (a) similar studies on anion complexation and (b) grafting various functionalities mixed with *N*-(1-pyrenylmethyl)acetamide functions to find new selectivities.

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11. *General*: Uncorrected melting points (Mps), Büchi 500. ^1H NMR and ^{13}C NMR, Varian (δ in parts per million from TMS, *J* in hertz). FAB-MS mass spectra, JEOL-JMS-HX 110A/110A High Resolution Tandem Mass Spectrometry in Korea Basic Science Institute (Korea). All the reactions were run under a nitrogen atmosphere. SiO_2 (Geduran 1.11567) was used for column chromatography. All reagents and solvents were commercial and used without further purification. Fluorescence spectra, RF-5301PC spectrofluorophotometer. Stock solutions (1.00 mM) of metal perchlorate salts were prepared in CH_3CN. Stock solutions of free **6**–**8** (0.060 mM) were prepared in $CHCl_3$. Excitations were carried out at 343 nm with all excitation and emission slit widths at 1.5 nm. Suitable crystal of **7** ($C_{89}H_{69}N_3O_9$) was mounted in air on a glass fibre tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 233(2) K.
Preparation of **2**. Calix[4]arene (1.00 g, 2.36 mmol), ethyl bromoacetate (0.39 g, 2.36 mmol), K_2CO_3 (0.16 g, 2.36 mmol) and CH_3CN (100 mL) were refluxed for 24 h. After removal of the solvent, the resulting solid was dissolved in CH_2Cl_2 and water. The organic layer was dried over anhydrous $MgSO_4$. After filtration, solvents were evaporated to give a solid, which was recrystallized from Et_2O to give pure **2** (0.72 g; 60% yields). Mp: 230–232 °C. ^1H NMR (200 MHz, $CDCl_3$): 9.88 (s, 1H, ArO*H*), 9.17 (s, 2H, ArO*H*), 7.12–6.99 (m, 8H, ArH_m), 6.70 (t, 1H, $J = 2.5$ Hz, ArH_p), 6.63 (t, 3H, $J = 2.5$ Hz, ArH_p), 4.88 (s, 2H, ArOCH_2CO$_2$Et), 4.48 (d, 2H, $J = 13.2$ Hz, ArCH_2Ar), 4.32 (d, 2H, $J = 13.2$ Hz, ArCH_2Ar), 4.30 (q, 2H, $J = 7.4$ Hz, ArOCH$_2$CO$_2$CH_2CH$_3$), 3.45 (d, 4H, $J = 13.2$ Hz, ArCH_2Ar), 1.43 (t, 3H, $J = 7.4$ Hz, ArCH$_2$-CO$_2$CH$_2$CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): 177.8, 169.5, 150.3, 149.7, 134.1, 129.5, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 126.2, 121.6, 121.0, 71.9, 62.0, **31.8**, **31.6**, 14.1 ppm. FAB-MS $m/z = 510.582$, calcd for $C_{32}H_{30}O_6$: 510.58. Anal. Calcd: C, 75.28; H, 5.92; O, 18.80. Found: C, 75.26; H, 5.95; O, 18.78.
Preparation of **3**. Same as for **2**. Calix[4]arene (5.00 g, 11.81 mmol), ethyl bromoacetate (9.84 g, 58.92 mmol), K_2CO_3 (4.91 g, 35.45 mmol) and CH_3CN (500 mL), reflux for 12 h. Recrystallized from Et_2O–MeOH (10/1) to give pure **3** (5.11 g, 57% yields). Mp: 235–237 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 6.64–6.61 (m, 12H, ArH_m and ArH_p), 4.78 (d, 4H, $J = 11.6$ Hz, ArCH_2Ar), 4.72 (s, 8H, ArOCH_2CO$_2$Et), 4.20 (q, 8H, $J = 4.8$ Hz ArOCH$_2$-CO$_2$CH_2CH$_3$), 3.24 (d, 4H, $J = 11.6$ Hz, ArCH_2Ar), 1.29 (t, 12H, $J = 4.8$ Hz, ArCH$_2$CO$_2$CH$_2$CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): 198.0, 170.1, 155.8, 134.6, 128.5, 122.8, 99.9, 71.2, 60.4, 56.2, 45.6, **31.4**, 28.7, 14.1 ppm. FAB-MS $m/z = 768.85$, calcd for $C_{44}H_{48}O_{12}$: 768.84. Anal. Calcd: C, 68.74; H, 6.29; O, 24.97. Found: C, 68.77; H, 6.32; O, 25.00.

Preparation of **4**. Compound **3** (1.00 g, 1.27 mmol), NaOH (0.250 g, 6.20 mmol), EtOH (10 mL), water (10 mL) and THF (4 mL) were refluxed for 12 h. After removal of the solvents the residue was dissolved in AcOEt and the solution was washed twice with 20% aqueous HCl and three times with water. The organic layer was dried over $MgSO_4$ and evaporated to give **4** (0.503 g, 59% yields). Mp: 170–171 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 6.50–7.12 (m, 12H, ArH_m and ArH_p), 4.14–4.66 (m, 20H, ArCH_2Ar, –OCH_2CO– and –CO$_2$$H$); ^{13}C NMR (200 MHz, $CDCl_3$): 217.2, 211.2, 197.8, 186.8, 185.1, 181.3, 177.6, 170.9, 162.2, 154.6, 152.1, 148.7, 134.2, 128.5, 127.9, 123.6, 112.0, 99.7, 71.9, 47.3, 40.5, 40.0, 39.6, 39.2, 38.8, **30.5**, 28.5, 23.3 ppm; FAB-MS $m/z = 656.60$, calcd for $C_{36}H_{32}OI_2$: 656.63. Anal. Calcd: C, 65.85; H, 4.91; O, 29.24. Found: C, 65.87; H, 4.88; O, 29.25.

Preparation of **6**. Same as for **2**. Compound **1** (1.00 g, 1.03 mmol), ethyl bromoacetate (0.52 g, 3.10 mmol), K_2CO_3 (0.30 g, 2.17 mmol) and CH_3CN (50 mL), reflux for 24 h. Column chromatography on silica gel using AcOEt–hexane (3/1) as eluent gave 0.505 g (41% yields) of **6** as a solid. Mp: 268–269 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 8.45 (t, 2H, $J = 3.7$ Hz, ArCONHCH$_2$–), 8.36–7.87 (m, 18H, ArH, pyrene), 6.98–6.90 (m, 8H, ArH_m), 6.94 (t, 2H, $J = 7.2$ Hz, ArH_p), 6.36 (t, 2H, $J = 7.2$ Hz, ArH_p), 5.37 (d, 4H, $J = 3.7$ Hz, –NHCH_2–pyrene), 4.54 (d, 4H, ArCH_2Ar, $J = 12.8$ Hz), 4.47 (s, 4H, ArOCH_2-CONH–), 4.44 (s, 4H, ArOCH_2CO$_2$Et), 3.30 (d, 4H, ArCH_2Ar, $J = 12.8$ Hz), 3.81 (q, 4H, $J = 6.1$ Hz, ArOCH$_2$CO$_2$CH_2CH$_3$), 1.53 (t, 6H, $J = 6.1$ Hz, ArOCH$_2$-CO$_2$CH$_2$CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): 178.2, 170.0, 149.4, 140.3, 134.5, 133.0, 132.7, 132.6, 131.8, 128.5, 126.0, 124.8, 76.7, 47.9, **31.9**, 25.4, 11.6 ppm; FAB-MS $m/z = 1139.27$, calcd for $C_{74}H_{62}N_2O_{10}$: 1139.29. Anal. Calcd: C, 78.01; H, 5.49; N, 2.46; O, 14.04. Found: C, 78.03; H, 5.45; N, 2.47; O, 14.02.

Preparation of **7**. Same as for **2**. Compound **2** (0.508 g, 0.98 mmol), *N*-(1-pyrenylmethyl)chloroacetamide (0.93 g, 3.02 mmol), K_2CO_3 (0. 68 g, 4.9 mmol), an excess NaI and CH_3CN (100 mL), reflux for 24 h. Chromatography on SiO_2 with AcOEt–hexane (3/1) as eluent to give 0.84 g (65% yields) of pure **7** as a white solid. Mp: 158–160 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.35 (broad t, 3H, $J = 3.6$ Hz, –CONH–), 8.17–7.25 (m, 27H, ArH, pyrene), 6.90–6.86 (m, 4H, ArH_p), 6.69–6.27 (m, 8H, ArH_m), 5.20 (dd, 2H, $J = 12.5$ Hz, $J = 3.6$ Hz, –CONHCH_2pyrene), 4.91 (dd, 2H, $J = 12.5$ Hz, $J = 3.6$ Hz, –CONHCH_2pyrene), 4.55 (s, 2H, –CONHCH_2pyrene), 4.47 (d, 2H, $J = 10.4$ Hz, ArOCH_2CONH–), 4.39 (d, 2H, $J = 10.4$ Hz, ArOCH_2CONH–), 4.29 (d, 2H, $J = 14.00$ Hz, ArCH_2Ar), 4.25 (d, 2H, $J = 14.00$ Hz, ArCH_2Ar), 4.60 (s, 2H, ArOCH_2CONH–), 4.10 (s, 2H, ArOCH_2CO$_2$Et), 3.49 (q, 2H, $J = 6.0$ Hz ArCH$_2$CO$_2$CH_2CH$_3$), 3.12 (d, 2H, $J = 14.00$ Hz, ArCH_2Ar), 2.91 (d, 2H, $J = 14.00$ Hz, ArCH_2Ar), 1.27 (t, 3H, $J = 6.0$ Hz ArCH$_2$CO$_2$CH$_2$CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): 169.3, 131.3, 131.0, 130.5, 130.4, 128.4, 127.7, 127.1, 125.8, 125.7, 125.0, 124.4, **31.8**, **31.6**, 14.1 ppm. FAB-MS $m/z = 1324.54$, calcd. for $C_{89}H_{69}N_3O_9$: 1324.51. Anal. Calcd: C, 80.71; H, 5.25; N, 3.17; O, 10.87. Found: C, 80.74; H, 5.27; O, 10.89.

Preparation of **8**. Compound **4**: (350 mg, 0.53 mmol), $SOCl_2$ (3 mL) and toluene (5 mL) were refluxed for 4 h. The $SOCl_2$ and toluene were removed by distillation. The residue was dissolved in THF and the solution was evaporated to remove the residual $SOCl_2$. The resulting solid **5** was used directly for amidation. Acyl chloride **5**, 1-pyrenylmethylamine hydrochloride (0.64 g, 2.39 mmol), NEt_3 (0.542 g, 5.33 mmol) and THF (20 mL) were refluxed for 2 days. After removal of the solvents, the resulting solid was dissolved in CH_2Cl_2 (100 mL) and water (100 mL). The organic layer was washed three times with water, dried over $MgSO_4$, filtered and evaporated to give a white solid, which was recrystallized from Et_2O to give 0.301 mg (37% yields) of pure **8**. Mp: 164–167 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.40 (broad t, 4H, $J = 3.5$ Hz, CONHCH$_2$–), 8.03–7.47 (m, 36H, ArH, pyrene), 6.50–6.17 (m, 12H, ArH_m and ArH_p), 5.12 (d, 8H, $J = 3.5$ Hz, –NHCH_2pyrene), 4.47 (s, 8H, –OCH_2CONH–), 4.29 (d, 4H, $J = 11.4$ Hz ArCH_2Ar), 3.16 (d, 4H, $J = 11.4$ Hz, ArCH_2Ar). ^{13}C NMR (200 MHz, $CDCl_3$): 198.0, 177.9, 134.7, 131.0, 128.4, 128.1, 127.7, 127.1, 125.7, 125.0, 124.5, **31.5**, 28.7. FAB-MS $m/z = 1509.77$, calcd for $C_{104}H_{76}N_4O_8$: 1509.74. Anal. Calcd: C, 82.74; H, 5.07; N, 3.71; O, 8.48. Found: C, 82.76; H, 5.10; N, 3.68; O, 8.45.

12. Crystal data for **7**: $C_{89}H_{69}N_3O_9$, triclinic, space group $P-1$, $a = 16.390(5)$, $b = 16.692(5)$, $c = 17.133(5)$ Å, $\alpha = 114.490(6)$, $\beta = 101.828(7)$, $\gamma = 110.302(6)°$, $V = 3651.3(19)$ Å^3, $D = 1.205$ g/cm^3, $\mu = 0.078$ mm^{-1}, $F(000) = 1392$. $R_1 = 0.1577$, $wR_2 = 0.4145$. Crystal data was deposited in the Cambridge Crystallographic Data Centre, under reference CCDC No. 283473.
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