Multiple Structures in Supramolecular Solids: Benzophenone Embedded in Three Different *C*-Methylcalix[4]resorcinarene/bipyridine Frameworks

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ABSTRACT: Three different supramolecular frameworks based on *C*-methylcalix[4]resorcinarene (CMCR) and 4,4′-bipyridine are described. All contain benzophenone molecules as guests and are prepared by almost identical hydrothermal procedures, indicating that variations during the cooling process, rather than templating, can lead to different phases. The benzophenone molecules show significantly different conformations, with energies calculated to be 10−17 kJ/mol higher than that of the isolated benzophenone molecule. CMCR exhibits chair, boat, and crown-like conformations in the three solid phases.

With the advance of very bright third-generation synchrotron sources, analysis of the structure of excited states of molecules is becoming a realistic possibility.[1] It is therefore necessary to identify systems suitable for such studies. Host/guest systems in which a photoactive molecule is embedded in an inert matrix are attractive, as the concentration of the active species is reduced, which means that fewer photons are required to achieve a certain conversion percentage and that the excited molecules are more widely spaced, making triplet−triplet annihilation less likely.

A number of different frameworks formed by *C*-methylcalix[4]resorcinarenes (CMCR) and bifunctional "pillar" molecules such as bipyridine and *trans*-bis(4-pyridyl)-ethylene[2] have been shown to contain large cavities capable of including organic or inorganic guests. Three different kinds of host structures formed by CMCR and bipyridine, capable of including guest molecules, have been described in the literature: a 0D carcerand-like capsule,[3] a 1D wave-like polymer,[4] and a 2D brick-wall-like sheet.[5]

We have recently described a novel stepped-sheet framework of the same building blocks, although different composition, which can similarly accommodate guest molecules.[2] In the three-dimensional network of CMCR·3bipy·benzophenone·2H$_2$O (**1**) (Figure 1), each CMCR molecule adopts a chair conformation[2] and is linked to adjacent CMCRs through hydrogen-bonded water molecules to form a column parallel to the crystallographic [010] direction. The four axial phenoxyl groups form O−H···N hydrogen bonds with bipyridine molecules, which link the columns into stepped sheets parallel to the (011) plane. These sheets are further connected by another bipyridine via O−H···N hydrogen bonds, giving rise to a three-dimensional network and leaving large channels in which the guest benzophenone molecules are included.

The size of the cavity in the CMCR frameworks can be adjusted to the guest molecules through the formation of different backbones or alteration of the support spacer.[6] We here report on two additional host−guest compounds based on benzophenone, CMCR, and bipy: CMCR·bipy·benzophenone·H$_2$O (**2**) and CMCR·2bipy·benzophenone (**3**), prepared under very similar crystallization conditions.

The existence of three different frameworks with the same building blocks, illustrates the remarkable versatility of CMCR based supramolecular solid-state structure.

Compounds **1**−**3** are synthesized by hydrothermal synthesis under essentially identical conditions.[7] Low-temperature X-ray analysis of a crystal of **2**[8] shows the CMCR molecules to be linked into columns by intermolecular hydrogen bonds [O2···O8a = 2.806(2) Å, O2−H2···O8a = 141(4)°; O5···O7b = 2.759(2) Å, O5−H5···O7b = 174(5)°; O6···O4b = 2.791(2) Å, O6−H6···O4b = 169(3)°; O8···O2a = 2.806(2) Å, O8−H8···O2a = 144(4)°; O1···O3 = 2.726(2) Å, O1−H1···O3a = 174(3)°; O7···O5b = 2.759(2) Å, O7−H7···O5b = 130(4)°; a −x, −y+1, −z; b −x+1, −y, −z+1]. In contrast to **1**, no water molecules are incorporated in the columns of **2**. As shown in Figure 2, the columns are connected by the bipy molecules, through O−H···N hydrogen bonding, into "skewed-brick" sheets parallel to the (011) plane, [O4···N1 = 2.690(2) Å, O4−H4···N1 = 170(3)°; O3···N2a = 2.711(2) Å, O3−H3···N2a = 169(3)°; a −x−1, −y+1, −z+1]. The arrangement is similar to that found in 2CMCR·4bipy·DMR, in which two CMCRs in adjacent columns are connected by pairs of stacked bipy dimers.[5] In **2**, however, CMCR molecules are connected by two bipy monomers, with a large space remaining between the monomers. Successive CMCR·bipyridyl layers are offset with respect to each other, such that cavities rather than channels are formed. Two benzophenone guests and two water molecules are incorporated in the cavities.

In the framework of **3**, CMCR molecules along the rim of a macrocycle form intramolecular hydrogen bonds [O3···O2 = 2.719(4) Å, O3−H3···O2 = 164(5)°; O4···O1b = 2.735(4) Å, O4−H4···O1b = 168(4)°; b x, −y+1/4, −z+1/4] (Figure 3a). Stacked bipy dimers connect two CMCR molecules in head-to-head fashion through hydrogen bonds [O1···N1a = 2.676(4) Å, O1−H1···N1a = 156(4)°; O2···N2 = 2.631(4) Å, O2−H2···N2 = 176(4)°; a −x+1/4, y, −z+1/4], thus forming a carcerand-like capsule, centered at a position with 222 symmetry in the *Fddd* space group. Two benzophenone molecules, each disordered across a 2-fold axis, are encapsulated in the cavity. The architecture is almost identical to that observed for the CMCR·2bipy·nitrobenzene solid, in which two disordered nitrobenzene molecules are included in the cavities.[3] As judged by the intermolecular distances between the opposing oxygen atoms in the two crown-shapes CMCR molecules (12.2 Å),

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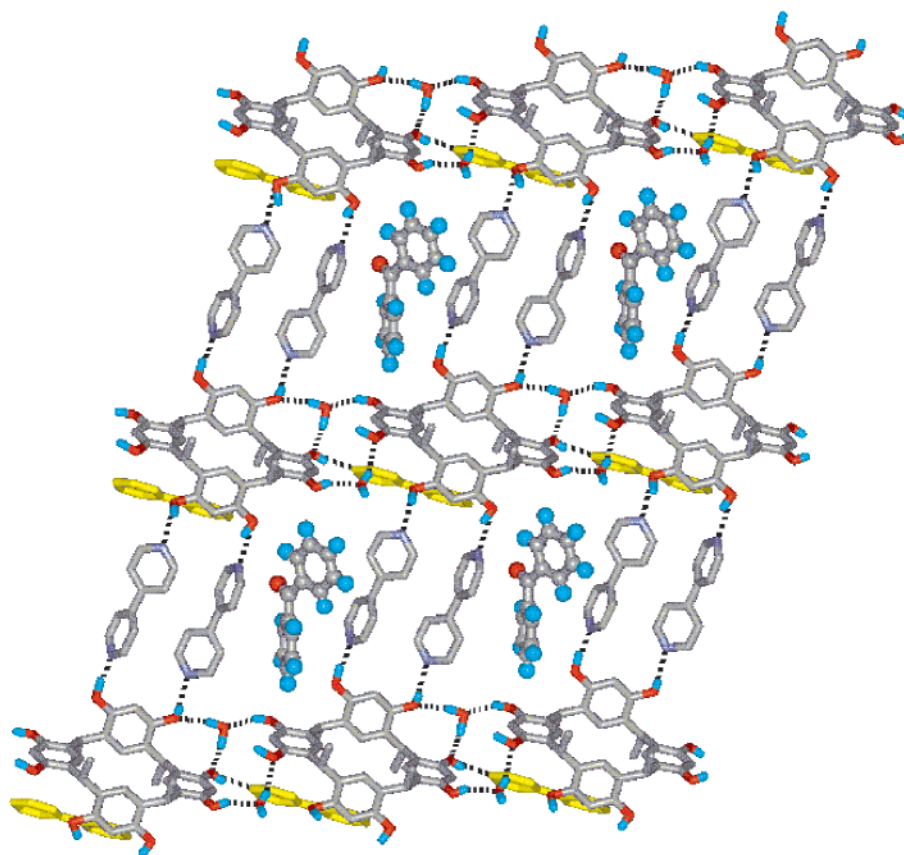* To whom correspondence should be addressed. E-mail: coppens@acsu.buffalo.edu.

Figure 1. The three-dimensional stepped sheet hydrogen-bonded network of **1** formed by CMCR, bipyridine, and the water molecules, showing benzophenone inside the channel.
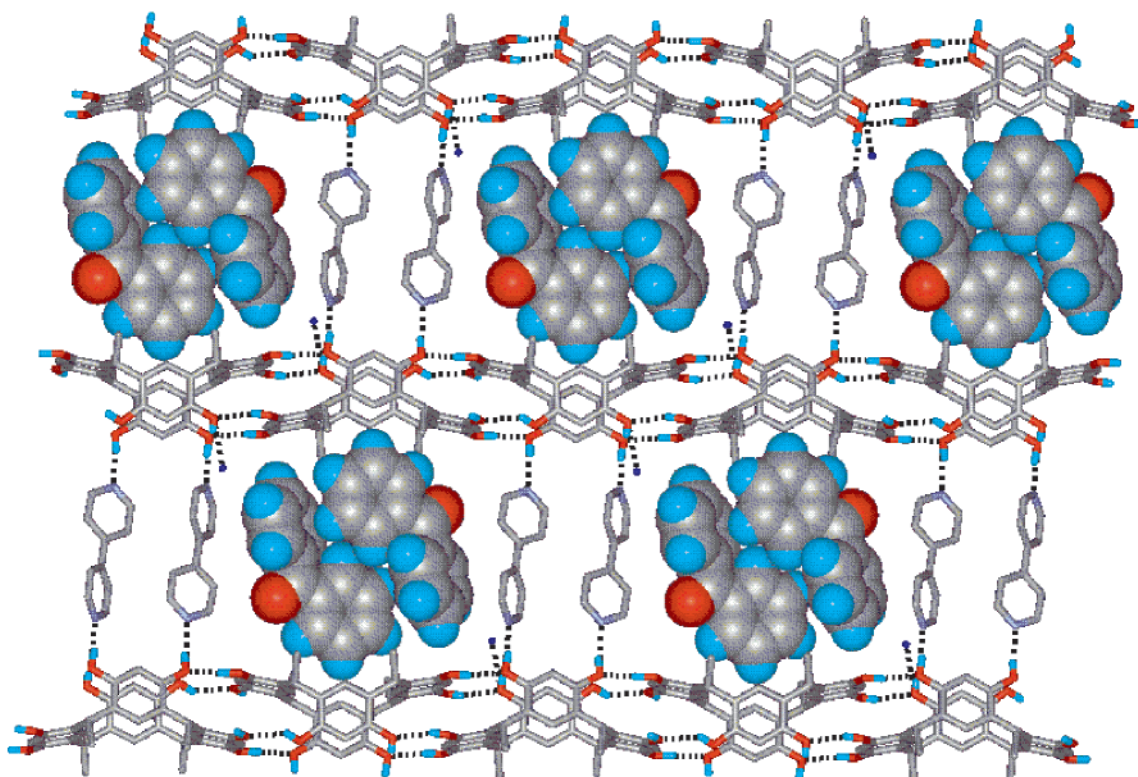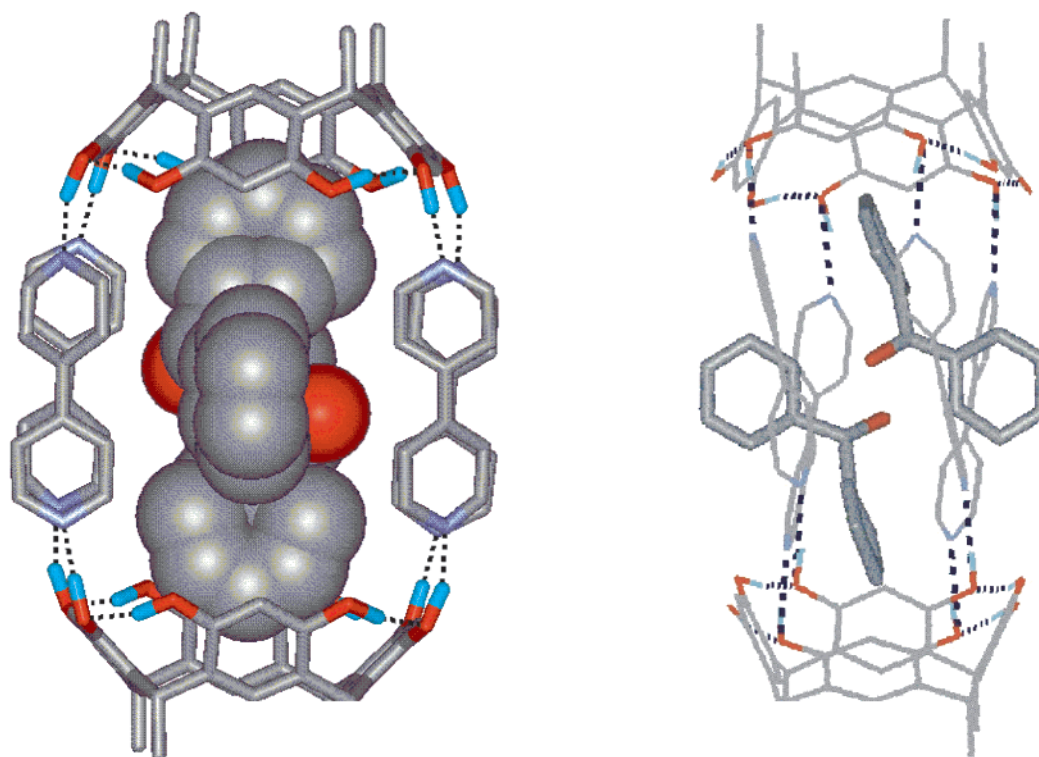
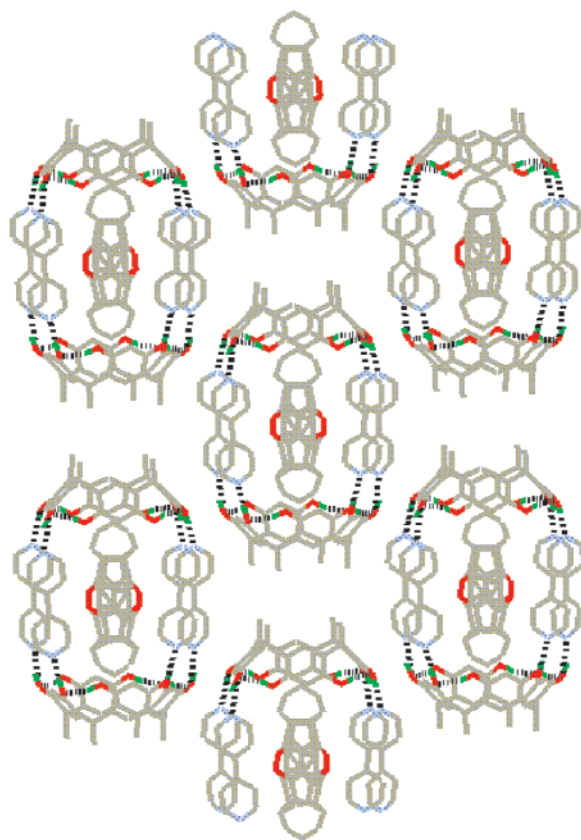Ⓦ A 3D rotatable image in XYZ format is available.

Figure 2. The two-dimensional hydrogen-bonded brick-wall sheet of **2** produced by CMCR and bipyridine, showing benzophenone within the cavity.

Ⓦ A 3D rotatable image in XYZ format is available.

(a)

(b)

Figure 3. (a) Two different views of the carcerand-like capsule in **3**, formed by hydrogen bonding between CMCR and bipyridine. The capsule has the crystallographic point-symmetry 222. The two benzophenone molecules included in the cavity each occupy two disordered positions related by one of the 2-fold axes. Only one of the positions for each is shown. (b) The face-centered packing of the capsules in the ab plane. Successive sheets are stacked into a three-dimensional face-centered arrangement.

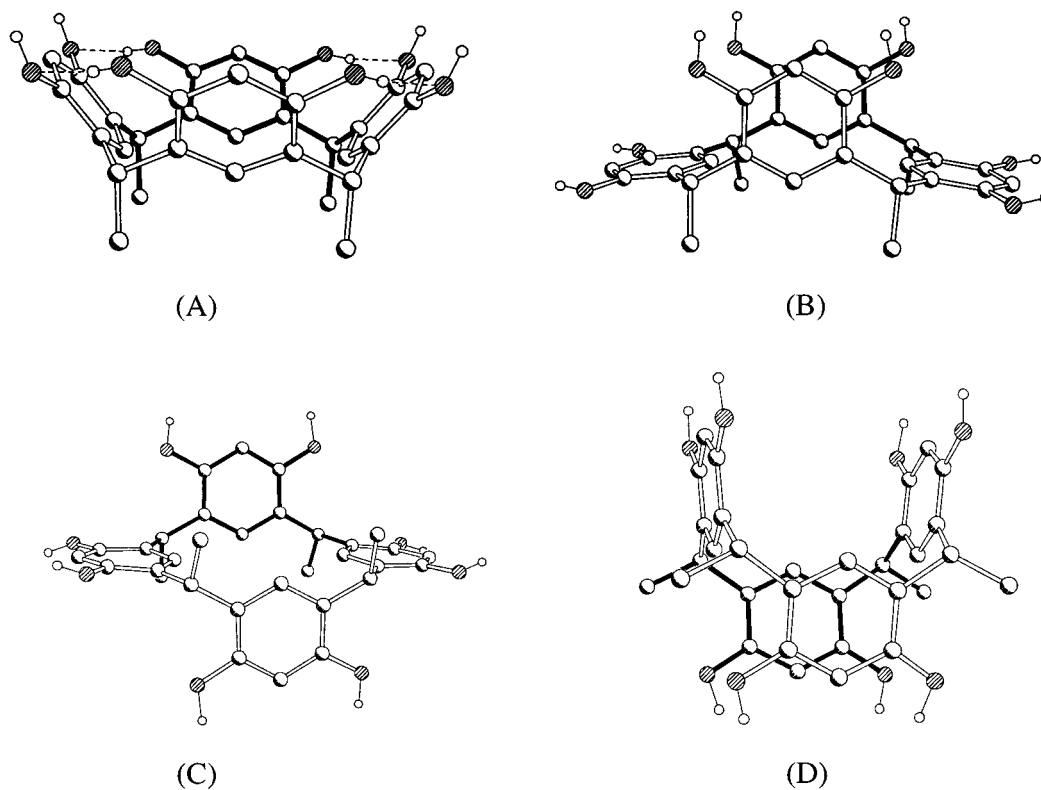Ⓦ 3D rotatable images of Ⓦ (a) and Ⓦ (b) in XYZ format are available.

Figure 4. Schematic drawing of the four conformations of *C*-methylcalix[4]resorcinarene: (A) crown; (B) boat; (C) chair; (D) saddle.

Table 1. Comparison of Concentration, Cavity Size, and Twist Angles of Benzophenone in the Gas Phase (theory), the Neat Crystal, and Host–Guest Compounds 1–3

comp	frame-work	conform for CMCR	conc (M/L)	cavity size/ guest molec (Å³)	twist angles (°)
isolated molec (calc)					30.70
α-benzo-phenone			6.64	47.58	31.0, 28.7[15]; 30.8, 30.0[16]
β-benzo-phenone			6.66	51.77	29.3, 43.5[17]
1	stepped sheet	chair	1.07	42.85	29.3, 16.7
2	brick-wall	boat	1.54	42.71	37.8, 18.5
3	carce-rand	crown	1.24	63.39	46.2, 7.7

the cavity size is the same in the two structures. The capsules are packed in a three-dimensional face-centered arrangement (Figure 3b), corresponding to the face-centering of the *Fddd* space group. The structure may be

described as a close-packed arrangement of approximately ellipsoidal capsules, not unlike the closed-packed structures often encountered for much simpler solids.

Thus, in the three supramolecular solids the benzophenone guest molecules are entrapped in a three-dimensional "stepped sheet", a two-dimensional "brick wall", and a zero-dimensional "carcerand-type" host framework. Although it is common that one framework includes different guests, the occurrence of one guest in three different host frameworks based on the same building blocks has, to our knowledge, not been observed previously. It is commonly assumed that the templating function of the guest molecules and the nature of the solvent play an important role in determining the host framework.[9] The generation of three different frameworks from reaction mixtures of identical composition indicates that the self-assembly of supramolecular frameworks is very much dependent on the conditions during crystal growth. While we do not believethat in the current case the replacement of air by argon gas plays a defining role, it is clear that the conditions during the hydrothermal synthesis process vary with time. It is quite likely that the different phases were formed at different times during the cooling stage following the warm-

Table 2. Summary of Theoretical Calculations on the Benzophenone Molecule in Different Conformations[a]

	total energy (kJ/mol)	difference (kJ/mol) relative to A(HF) or B(DFT)	dipole moment (D)	twist angle (°)	dihedral angle (°)
benzophenone isolated molecule	−1504709 (A)		3.24	30.70	55.66
(optimized)	−1514336 (B)		3.14	28.92	52.54
β-benzophenone[b]	−1504697	12	3.65	29.27	64.54
	−1514324	12	3.33	43.49	
CMCR·bipy·benzophenone·H₂O **2**	−1504693	16	3.54	18.51	52.41
	−1514326	10	3.24	37.55	
CMCR·3bipy·benzophenone·2H₂O **1**	−1504692	17	3.33	16.69	42.01
	−1514325	11	3.05	29.28	

[a] The twist angles are defined as the dihedral angle between the C(C=O)C plane and the plane of the phenyl ring. First line for each entry: HF, 6-311G**++ basis set; second line: DFT, B3LYP functional, 6-311G**++ basis set. [b] Conformation of α-benzophenone not calculated, because of lack of accuracy of the 1968 structures.

up in the sealed tubes. We are repeating the syntheses under carefully controlled temperature conditions to gain further insight into the factors governing the self-assembly in the course of hydrothermal synthesis.

Most interestingly, the CMCR exhibits chair, boat, and crown-like conformations in **1**–**3**, respectively, illustrating the adaptability of this molecule. Four types of conformations, illustrated in Figure 4, have been predicated by solution NMR methods.[10] The crown-like conformation has been observed several times in crystalline solids,[11] while the flattened cone, boatlike conformation has been found only recently in the solid state.[5,12] The chair conformation of CMCR was first observed in **1** and two related solids not containing guest molecules.[2] The saddle conformation remains undetected, at least by X-ray methods.

The twist angles between the CC=OC plane and two planes of phenyl ring of benzophenone for **1**–**3** show significant differences and are also different from those in the two phases of neat benzophenone (Table 1). Its variation in a wide range illustrates the adjustment of the benzophenone guest molecules to the constraints imposed by the framework. Energy differences between the different conformations, as calculated by Jaguar,[13] are relatively small and range 10–17 kJ/mol above the energy calculated for the isolated molecule (Table 2). The size of the cavity, as defined by Ohashi et al.,[14] is significantly larger per included molecule for the carcerand-type cavity of **3** than for **1** and **2** and for neat benzophenone. The larger space available in **3** may account for the observed guest-disorder in this solid. On the other hand, the cavity sizes for **1** and **2** are comparable and significantly smaller than those in neat benzophenone; thus, the guest will be fully restrained in these cases, in accordance with the observed lack of disorder. No relationship between the twist angles and the size of the cavity is evident.

We conclude that hydrothermal synthesis is a practical method for preparing CMCR supramolecular complexes. Three different frameworks based on bipyridine and CMCR with different conformations entrapping photoactive benzophenone guest have been prepared. The appreciable dilution of the photoactive guest achieved in the host–guest crystal (by a factor of 4–6) and the lack of guest-disorder in **1** and **2** make these two phases suitable candidates for photocrystallographic studies.

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(7) Compounds **1** and **2** were prepared as follows. An aqueous solution (4 mL) of *C*-methylcalix[4]resorcinarene (0.025 mmol), bipyridine (0.05 mmol) and benzophenone (0.05 mmol) was mixed and sealed in a heavy walled Pyrex glass tube (ca. 6 mL). The mixture was maintained at 140 °C for 1 day in an oven, and subsequently cooled to room temperature at a rate of 20 °C/day. Two kinds of crystals, colorless plates and light-yellow blocks, were separated and identified as **1** and **2**, respectively. Compound **3** was obtained by a similar procedure. An aqueous solution (4 mL) of *C*-methylcalix[4]resorcinarene (0.025 mmol), bipyridine (0.05 mmol), and benzophenone (0.05 mmol) was mixed and sealed in a heavy walled Pyrex glass tube with an argon atmosphere (ca. 6 mL). The tube was kept at 140 °C for 1 day in an oven, then cooled to room temperature at a rate of 20 °C/day. Light yellow block-shaped crystals were collected.
(8) Compound **2**: $C_{55}H_{52}N_2O_{10}$: $M_r = 900.99$, triclinic, space group P-1, $a = 10.0723(2)$, $b = 13.7350(3)$, $c = 17.3384(4)$ Å, $\alpha = 75.975(1)$, $\beta = 79.797(1)$, $\gamma = 68.858(1)$°, $U = 2159.81$-(8) Å^3, $Z = 2$, $Dc = 1.385$ Mg/m^3, Crystal size $0.48 \times 0.32 \times 0.24$ mm^3, μ (Mo–Kα) = 0.095 mm^{-1}, $F(000) = 952$, $GoF = 1.053$. Among 20 490 reflections, 11 109 reflections are unique ($R_{int} = 0.0317$). The final $R1$ and $wR2$ are 0.0574 and 0.1597, respectively, for 805 parameters and 7938 reflections [$I > 2\sigma(I)$]. Compound **3**: $C_{65}H_{58}N_4O_9$: $M_r = 1039.15$, Orthorhombic, space group $Fddd$, $a = 22.824(3)$, $b = 25.799(3)$, $c = 36.354(5)$ Å, $U = 21407(5)$ Å^3, $Z = 16$, $Dc = 1.290$ Mg/m^3, Crystal size $0.18 \times 0.12 \times 0.09$ mm^3, μ (Mo–Kα) = 0.086 mm^{-1}, $F(000) = 8768$, $GoF = 0.982$. Among 18 501 reflections, 6391 reflections are unique ($R_{int} = 0.0842$). The final $R1$ and $wR2$ are 0.0863 and 0.2177, respectively, for 453 parameters and 2912 reflections [$I > 2\sigma(I)$]. The data were collected on a Bruker SMART1000 CCD diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) at 90(1) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program.
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