Supramolecular Chemistry

Self-Assembly of Two Distinct Supramolecular Motifs in a Single Crystalline Framework**

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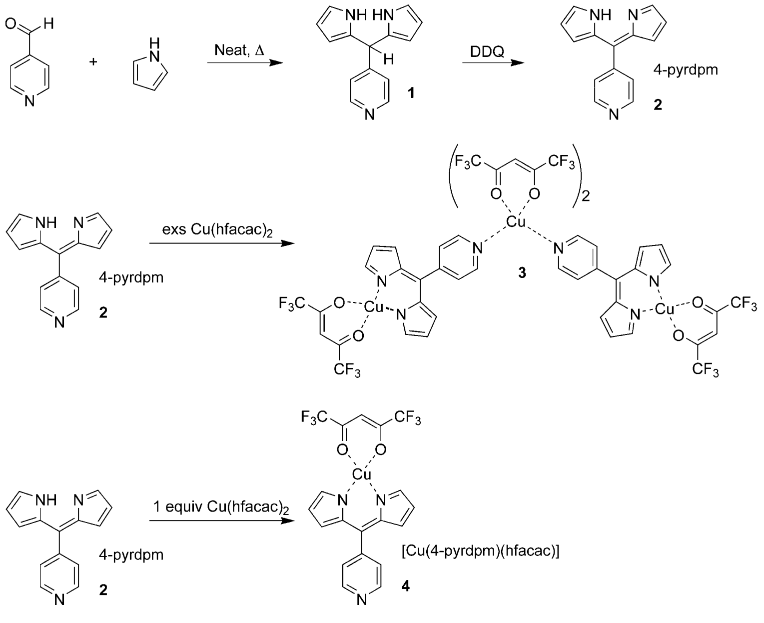
Supramolecular chemistry is a rapidly growing field of research concerned with the construction of molecular assemblies held together by noncovalent interactions.[1,2] Forces such as hydrogen bonding, π–π stacking, and metal–ligand coordination have been extensively used in the synthesis of supramolecular structures. These assemblies are anticipated to find utility as new materials with novel catalytic, magnetic, electronic, and optical properties.[3–6] Within the realm of supramolecular complexes that utilize metal–ligand interactions, both discrete molecular species and coordination polymers have been investigated. We are aware of only one case in which a reaction has yielded both a discrete complex and an extended polymeric structure from the same building block.[7] However, we know of no examples in which these two general topologies were found to co-exist in a stable crystalline solid. Herein, we report the synthesis of a self-assembling, self-complementary metal complex that forms a supramolecular hexagon and a double-helical coordination polymer within a single crystalline lattice. Furthermore, it is proposed that aggregation of fluorine substituents is a key feature in directing the formation of this surprising example of supramolecular assembly.

We have previously described heteroleptic copper(II) complexes with dipyrromethene (dipyrrin) ligands[8] that can form self-complementary, one-dimensional "zig-zag" coordination polymers.[9] These complexes consist of square-planar copper(II) centers bound by one dipyrrin ligand and one acetylacetonate (acac) ligand. The dipyrrin ligand features a second donor site (pyridyl nitrogen atom) that coordinates to the axial position of a neighboring copper(II) center, thereby generating an extended structure. In an effort to explore the features of these complexes that would alter the polymeric structure, modifications of the acac ligand were pursued. Instead of using Cu(acac)$_2$ as the copper source, Cu(hfacac)$_2$ (hfacac = hexafluoroacetononate) was utilized, which resulted in a heteroleptic metal complex with a "blocking" hfacac ligand (Scheme 1). This change in the spectator ligand was found to noticeably alter the complexation behavior and supramolecular assembly of the heteroleptic compound.

The products of the reaction between the dipyrrin ligand (4-pyrdpm = 5-(4-pyridyl)dipyrromethene, **2**) and Cu(hfacac)$_2$ were found to be dependent on the component stoichiometry (Scheme 1). In situ generation of **2** combined with an excess of Cu(hfacac)$_2$ results in the isolation of the



Scheme 1. Scheme for the synthesis of 4-pyrdpm (**2**) and heteroleptic copper complexes (**3** and **4**).

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trinuclear species **3**. This compound contains two distorted square-planar copper(II) complexes bound to an octahedral copper(II) center through the *meso*-pyridyl nitrogen-atom donors (Figure 1).[10] This species is not observed nor isolated under identical reaction conditions when employing Cu(acac)$_2$ as the starting material.[9] When 4-pyrdpm (**2**) is mixed with substoichiometric amounts of Cu(hfacac)$_2$, the expected mononuclear, heteroleptic complex [Cu(4-pyrdpm)(hfacac)] (**4**) can be isolated by flash silica chromatography in modest yield.

The solid-state structure of **4** was anticipated to yield a linear coordination polymer similar to that found for [Cu(4-pyrdpm)(acac)].[9] However, crystallization of **4** reveals a surprising structure in which the compound self-organizes into two distinct supramolecular motifs: a discrete molecular hexagon and a helical coordination polymer (Figure 2).[10] The supramolecular hexagon is comprised of six molecules of **4** tethered together by apical coordination of the *meso*-pyridyl nitrogen atoms (Cu-N$_{pyr}$ 2.28 Å).[11–18] The neighboring Cu–Cu distance is 9.72 Å, and the ring has a diameter of

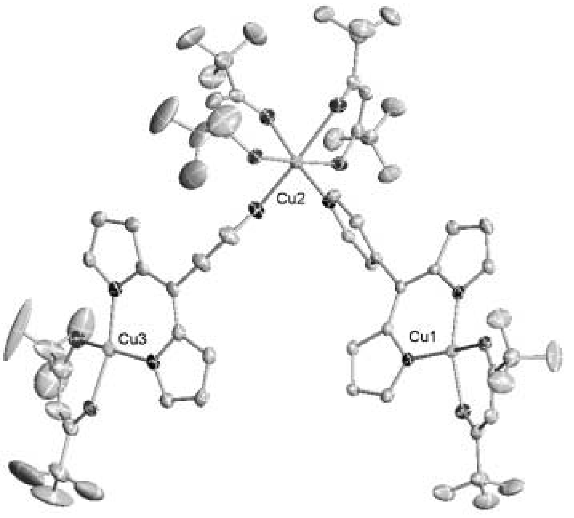

Figure 1. Structural diagram of trinuclear complex **3** with copper(II) atom numbering scheme (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.

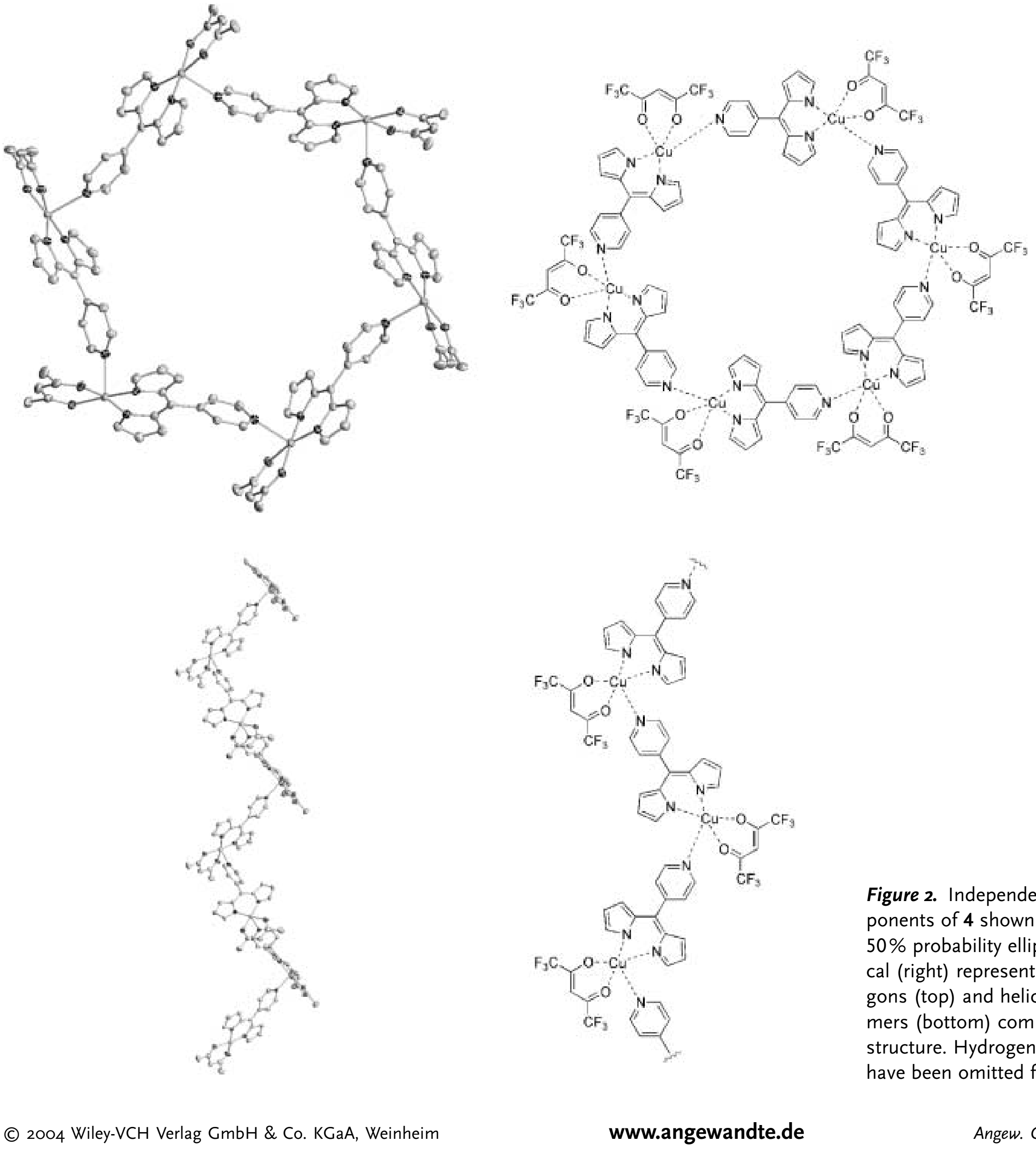

Figure 2. Independent crystallographic components of **4** shown in structural (ORTEP, 50% probability ellipsoids, left) and chemical (right) representations. Molecular hexagons (top) and helical coordination polymers (bottom) comprise the supramolecular structure. Hydrogen and fluorine atoms have been omitted for clarity.

about 19.24 Å (based on Cu–Cu distance of opposite metal centers on the ring), placing this among the largest neutral molecular hexagons characterized by single-crystal X-ray diffraction methods.[7] The cocrystallized helical coordination polymer[19–22] is also connected by apical coordination of pyridyl substituents (Cu-N_{pyr} 2.30 Å) in a manner generally consistent with related systems.[9,23]

A view along the crystallographic *c* axis shows the molecular hexagons lie in line with each other making hexagonal channels (Figure 3). The crystallographic data indicate that these channels are empty or only occupied by small amounts of highly disordered solvent molecules (two residual electron density peaks of $\approx 2.0\,e\,Å^{-3}$ suggest some disordered solvent may be present).[10] The individual metal complexes are neutral, therefore disqualifying the presence of counterions in the pores. Drying of the crystals under vacuum at 50 °C did not appear to disturb the crystal morphology and elemental analysis of the material was consistent with the absence of any cocrystallized solvent. Differential scanning calorimetry (DSC) reveals a single endotherm at 197 °C and thermogravimetric analysis (TGA) shows no weight loss up to about 200 °C. DSC and TGA of related compounds have clearly shown the presence of trapped solvent molecules[9] thereby supporting the contention that **4** does not contain significant amounts of solvent guests.

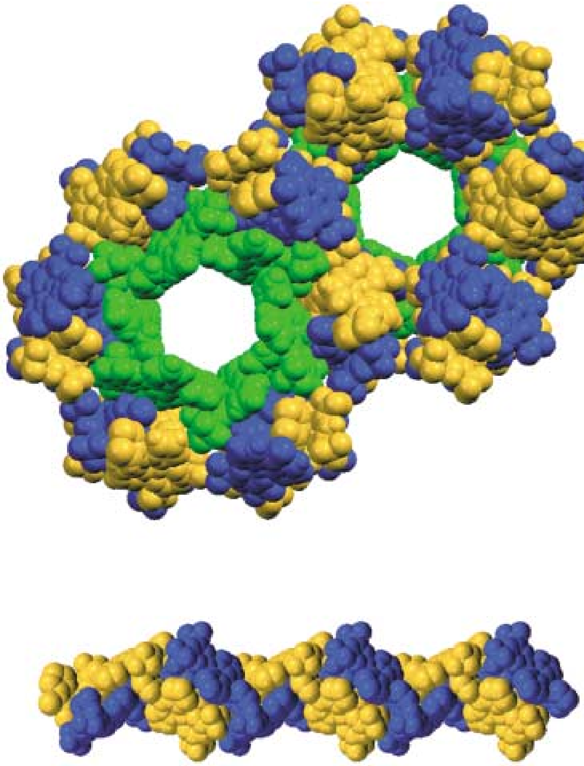

Figure 3. Spacefilling packing diagram for **4** (top) along the crystallographic *c*-axis. The hexagons are shown in green and the strands of the double-helices are shown in orange and blue. An isolated double-helix in **4** (bottom) viewed perpendicular to the crystallographic *c* axis.

Perhaps the most striking feature of **4** is the packing arrangement of the two supramolecular motifs within the crystalline lattice. Adjacent to each edge of the molecular hexagons are the coordination polymers, which run along the crystallographic *c* axis parallel to the hexagonal channels (Figure 3). The packing diagram reveals that the coordination polymers are more than simple helical chains; the strands arrange as pairs of antiparallel double helices.

The packing of the molecular hexagons with the double-helical coordination polymers suggests that the fluorine groups self-segregate from other parts of the structure to drive the formation of this elaborate assembly. The high immiscibility and hydrophobicity of the CF_3 group has been successfully utilized in the rational design of self-assembled peptide coiled coils.[24–26] In the structure of **4**, the hfacac ligands of the hexagon are interdigitated between the double-helices where they contact the hfacac ligands from the coordination polymer chains (Figure 4). The space between the helices is packed with CF_3 groups from both the hexagon and the polymers. The hfacac groups of the helices are in turn arranged to interact with one another, essentially creating

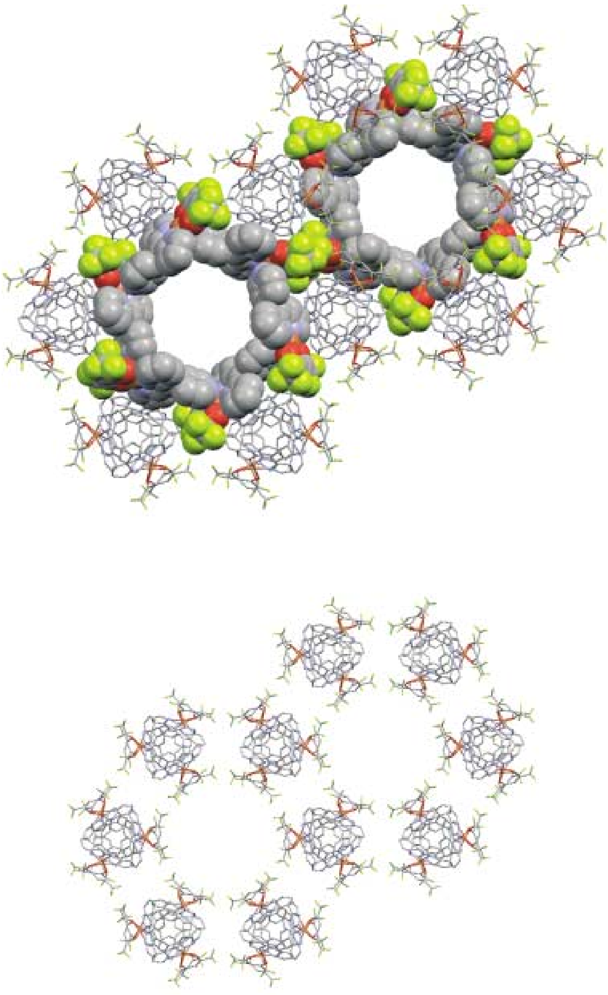

Figure 4. Packing diagram for **4** (top) along the crystallographic *c*-axis; hexagons are shown in spacefilling and double-helices are shown in stick form. Same view of **4** (bottom) with the hexagons removed. Hydrogen atoms have been removed for clarity.

rings of CF_3 groups periodically in the *c*-axis channels. The hexagonal channels are therefore composed of alternating layers of molecular hexagon "holes" and helical polymer "walls" that remain in register with each other (inner diameter ≈ 15.4 Å). Ultimately, the packing of the two supramolecular entities suggests separation of the fluorous phases drive the exotic solid-state arrangement of the assembly. This hypothesis is further supported by the observation that both [Cu(4-pyrdpm)(acac)] and [Cu(4-pyrdpm)(tfacac)] (tfacac = trifluoroacetononate) form simple, one-dimensional zig-zag coordination polymers.[9,23] Ongoing studies in our laboratory are focused on the host–guest chemistry and self-assembly of related complexes.

Experimental Section

$[Cu_3(4\text{-pyrdpm})_2(hfacac)_4]$ (**3**): 5-(4-Pyridyl)dipyrromethane (**1**)[9,27] (0.30 g, 1.34 mmol) was dissolved in $CHCl_3$ (150 mL) and stirred in an ice bath. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.31 g, 1.34 mmol) was dissolved in benzene (100 mL) and added dropwise. $Cu(hfacac)_2{\cdot}H_2O$ (0.64 g, 1.34 mmol) dissolved in $CHCl_3$ (50 mL) was added and stirred for 10 min to form the copper(II) complex. The reaction mixture was evaporated to dryness, and the product was purified by column chromatography (SiO_2; $CHCl_3$ with 1 % MeOH) to afford a red solid (0.27 g, 27 % yield). Elemental analysis (%) calcd for $C_{48}H_{24}F_{24}N_6O_8Cu_3{\cdot}0.5\,CHCl_3$: C 38.35, H 1.63, N 5.53; found: C 38.02, H 1.27 , N 5.56. UV/Vis (CH_2Cl_2): $\lambda_{max} = 232$, 304, 490 nm; IR (film from CH_2Cl_2): $\tilde{\nu} = 1644$, 1562, 1255, 1214, 1145, 1029, 1000 cm^{-1}. Red plates of **3** were grown from a solution of the complex in $CHCl_3$ diffused with pentane.

[Cu(4-pyrdpm)(hfacac)] (**4**): 5-(4-Pyridyl)dipyrromethane (**1**)[9,27] (0.30 g, 1.34 mmol) was oxidized as described for **3**. $Cu(hfacac)_2{\cdot}H_2O$ dissolved in 50 mL of $CHCl_3$ was added in small increments until all of the oxidized methene had been converted to the metal complex. The addition was monitored by using TLC and UV/Vis spectroscopy. The total added $Cu(hfacac)_2{\cdot}H_2O$ was 0.40 g (0.84 mmol, 0.63 equiv to **1**). The reaction mixture was evaporated to dryness and the product was purified by column chromatography (SiO_2; $CHCl_3$ with 1 % MeOH) to afford a red solid (0.15 g, 22 % yield). ESI-MS: *m/z* 490.9 $[M+H]^+$. Elemental analysis (%) calcd for $C_{19}H_{11}F_6N_3O_2Cu$: C 46.49, H 2.26, N 8.56; found: C 46.46, H 2.23, N 8.75. UV/Vis (CH_2Cl_2): $\lambda_{max} = 232$, 312, 492 nm; IR (film from CH_2Cl_2): $\tilde{\nu} = 1648$, 1560, 1252, 1209, 1144, 1030, 997 cm^{-1}. Red-green blocks of **4** were grown from a solution of the complex in $CHCl_3$ diffused with hexanes.

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[1] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, **2000**.

[2] J.-P. Sauvage, *Transition Metals in Supramolecular Chemistry, Vol. 5*, Wiley, New York, **1999**.

[3] O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474.

[4] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[5] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.

[6] E. G. Tulsky, J. R. Long, *Chem. Mater.* **2001**, *13*, 1149.

[7] H. Abourahma, B. Moulton, V. Kravtsov, M. J. Zaworotko, *J. Am. Chem. Soc.* **2002**, *124*, 9990.

[8] S. R. Halper, S. M. Cohen, *Chem. Eur. J.* **2003**, *9*, 4661.

[9] S. R. Halper, M. R. Malachowski, H. M. Delaney, S. M. Cohen, *Inorg. Chem.* **2004**, *43*, 1242.

[10] CCDC 225998 (**3**) and CCDC 225999 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). Also see Supporting Information.

[11] B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956.

[12] P. J. Stang, N. E. Persky, J. Manna, *J. Am. Chem. Soc.* **1997**, *119*, 4777.

[13] T. Yamamoto, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 12309.

[14] G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush, P. S. Russo, *Angew. Chem.* **1999**, *111*, 3899; *Angew. Chem. Int. Ed.* **1999**, *38*, 3717.

[15] Y. L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin, K.-S. Jeong, *J. Am. Chem. Soc.* **2001**, *123*, 1258.

[16] M. M. Ali, F. M. MacDonnell, *J. Am. Chem. Soc.* **2000**, *122*, 11527.

[17] R. Takahashi, Y. Kobuke, *J. Am. Chem. Soc.* **2003**, *125*, 2372.

[18] D. T. Puerta, S. M. Cohen, *Chem. Commun.* **2003**, 1278.

[19] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584; *Angew. Chem. Int. Ed.* **1999**, *38*, 492.

[20] O. Mamula, A. von Zelewsky, T. Bark, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 3129; *Angew. Chem. Int. Ed.* **1999**, *38*, 2945.

[21] J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem.* **1999**, *111*, 3707; *Angew. Chem. Int. Ed.* **1999**, *38*, 3498.

[22] C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970; *Angew. Chem. Int. Ed.* **1998**, *37*, 920.

[23] S. R. Halper, S. M. Cohen, unpublished results.

[24] B. Bilgiçer, X. Xing, K. Kumar, *J. Am. Chem. Soc.* **2001**, *123*, 11815.

[25] B. Bilgiçer, A. Fichera, K. Kumar, *J. Am. Chem. Soc.* **2001**, *123*, 4393.

[26] E. N. G. Marsh, *Chem. Biol.* **2000**, *7*, R153.

[27] P. D. Rao, S. Dhanalekshmi, B. J. Littler, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 7323.