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One-Dimensional Cadmium Polymers with Alternative di(EO/EE) and di(EO/EO/EO/EE) Bridged Azide Bonding Modes

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S *Supporting Information*

ABSTRACT: Four new doubly bridged Cd(II)-azido complexes derived from sterically hindered NNN- and NN-donors were synthesized and structurally characterized. The tridentate amine ligands 2-methylquinolyl-2(ethyl-2-pyridyl)-methyl-amine (Meepmqa) and bis(2-methylypyridyl)methylamine (MeDPA) afforded the dinuclear complexes $[Cd_2(Meepmqa)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$ (**1**) and $[Cd_2(MeDPA)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**2**) with di-EE- and di-EO-azido bridges, respectively. The N-substituted trialkyl ethyl-enediamine compounds N,N,N'-triethylethylenediamine (Et$_3$en) and N,N,N'-trimethylethylenediamine (Me$_3$en) resulted in the formation of 1D-polymeric chains $\{[Cd_2(Et_3en)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)_2]\}_n$ (**3**) and $\{[Cd_4(Me_3en)_4(\mu_{1,1}\text{-}N_3)_6(\mu_{1,3}\text{-}N_3)_2]\}_n$ (**4**) with alternative (di-EO/di-EE)- and di(EO/EO/EO/EE)-azido bonding modes. The IR asymmetric stretching vibration, $\nu_{as}(N_3)$ of the azido ligands in these complexes and in related complexes, were analyzed in an attempt to predict the coordination bonding mode of the bridged azide. The fluorescence properties of the ligand Meepmqa and its complex **1** are reported. The Cd-complex **1** has increased fluorescence intensity compared to its free ligand. This was attributed to the strong Cd−N bond of the quinolyl group of Meepmqa and the nonflexibility of the corresponding five-membered chelate ring.
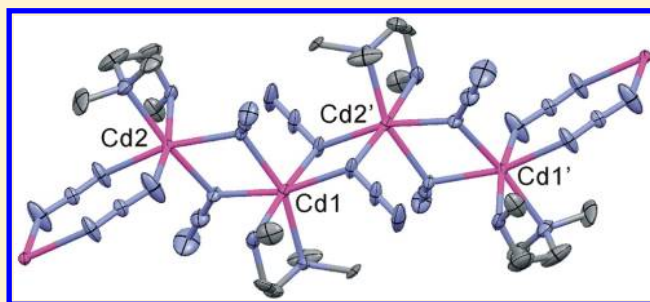
INTRODUCTION

Azide ion, N_3^-, is a flexidentate ligand that can simultaneously bind several metal ions in different coordination modes. The potential affinity of this small ion to act as a bridging linker and to assemble metal ions in 1-, 2-, or 3-D extended polymeric networks has led to the isolation of a number of coordination compounds with interesting molecular and crystalline architectures.[1−15] In addition to this, the bridged azide anion serves as an excellent effective ligand to propagate the magnetic interaction between the paramagnetic centers where magnetic superexchange mechanism is known to occur through various modes.[1−15] All these properties made this ligand an attractive target for extensive studies. Thus, aside from the terminal mondentate nature of the azido ligand, many bridging coordination modes such as single- and double-bridges $\mu_{1,3}$-N_3 (end-to-end, EE),[1−7] $\mu_{1,1}$-N_3 (end-on, EO),[1−3,6−8] and ($\mu_{1,3}$-N_3)/($\mu_{1,1}$-N_3) (EE/EO),[16] triple-bridges[13,14] $\mu_{1,1,3}$-N_3 and $\mu_{1,1,1}$-N_3, quarterly bridges[13−15] $\mu_{1,1,1,1}$-N_3 and $\mu_{1,1,2,2}$-N_3, and hexa-bridges $\mu_{1,1,1,3,3,3}$-N_3 were also reported.[9,13−16] Alternative $\mu_{1,3}$-N_3 and $\mu_{1,1}$-N_3 bridges were also found in some systems.[6d,e,8b,9a,10,11,14] Scheme 1 summarizes only the different modes of mono and doubly bridged azide as assembled by two metal ions in dinuclear and/or in polynuclear species. The type and the topological features of the resulting coordination complexes depend largely on the nature of the coordinated coligands and the steric environment imposed by these ligands, and to some extent on the nature of the central metal ion, its oxidation state and coordination number as well as on the geometry of the complex.[1,2,17]

Cadmium(II)−pseudohalides, specifically Cd(II)−N$_3$, are of particular interest not only in the synthesis of polynuclear[1,16−19] and polymeric compounds with different dimestionality,[20−28] but also in their ability to affect the emission wavelength.[19,20c,28−30] Some of these compounds produced interesting structures with different alternative bonding modes of azide bridges (structure **VI** in Scheme 1).[25−29] Similar structures were reported in azido-Cu(II) and -Ni(II) complexes, which were derived from sterically hindered coligands.[10−12,16] As a d^{10} metal ion, the Cd(II) ion in certain complexes can enhance or quench the fluorescence emission of the organic ligand.[19,27] The fluorescence's enhancement in the Cd(II)−azido complexes is more interesting from the photochemical applications point of view. The photoinduced electron transfer (PET) process results from the excitation of the lone-
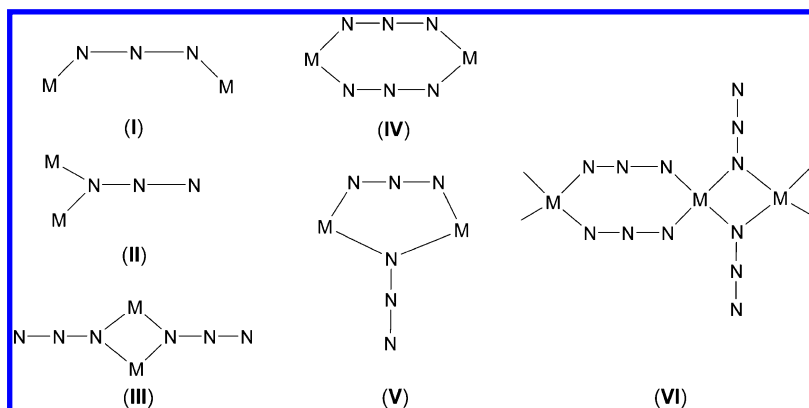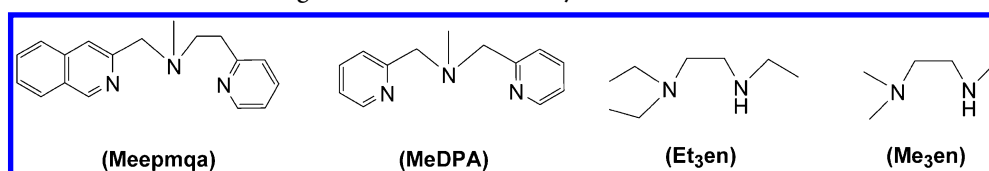
Scheme 1. Different Azido Bridging Modes with the Azide Anion Binding Two Metal Ions

Scheme 2. Structure Formulas of Amine Ligands Used in This Study

(Meepmqa)   (MeDPA)   (Et₃en)   (Me₃en)

pairs of electrons, which are located in the donor atoms of the ligand. This process may be prevented or the fluorescence intensity may be enhanced upon complexation of the ligand with metal ions.[19,20c,27−30]

Herein, we present the synthesis and structural studies of four new doubly bridged Cd(II)−azido complexes: with tridentate amine ligands, the dinuclear complexes $[Cd_2(Meepmqa)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$ **(1)** and $[Cd_2(MeDPA)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ **(2)** with di-EE- and di-EO-azido bridges, respectively, and the 1D-polymeric chains $\{[Cd_2(Et_3en)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)_2]\}_n$ **(3)** and $\{[Cd_4(Me_3en)_4(\mu_{1,1}\text{-}N_3)_6(\mu_{1,3}\text{-}N_3)_2]\}_n$ **(4)** with alternative (di-EO/di-EE)- and di(EO/EO/EO/EE)-azido bonding modes. The fluorescence properties of complex **1** was also examined. The structure formulas of the ligands, 2-methylquinolyl-2(ethyl-2-pyridyl)-methylamine (Meepmqa), bis(2-methylypyridyl)methylamine (MeDPA), N,N,N′-triethylethylenediamine (Et₃en), and N,N,N′-trimethylethylenediamine (Me₃en) are presented in Scheme 2.

■ EXPERIMENTAL SECTION

Materials and Physical Measurements. 2-Chloromethylquinoline hydrochloride, dipicolylamine (DPA), N,N,N′-triethylethylenediamine (Et₃en), and N,N,N′-trimethylethylenediamine (Me₃en) were purchased from TCI-America, whereas 2-[2-methylaminoethyl]-pyridine was purchased from Maybridge Co., Belgium. Infrared spectra were recorded on JASCO FT/IR-480 plus spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker 400 MHz NMR spectrometer operating at 400 (^{1}H) and 100 MHz (^{13}C). ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in ppm and were referenced internally to residual solvent resonances (d_6-DMSO: $\delta_H = 2.49$, $\delta_C = 39.4$ ppm). ESI-MS was measured on LC−MS Varian Saturn 2200 Spectrometer. Fluorescence measurements were performed on a Perkin-Elmer LS50 spectrometer. Elemental analyses were carried out by the Atlantic Microlaboratory, Norcross, Georgia USA.

Caution: Salts of perchlorate and azide as well as their metal complexes are potentially explosive and should be handled with great care and in small quantities.

Synthesis of the Compounds. *Synthesis of 2(2-ethylpyridyl)-(2-methylquinolyl)-methylamine (Meepmqa).* 2-(2-Methylaminoethyl)-pyridine (1.36 g, 10 mmol) was added to a suspension of 2-chloromethylquinoline hydrochloride (2.14 g, 10 mmol) in dry THF (30 mL). To this, anhydrous CsCO₃ (8.15 g, 20 mmol) was added, and the resulting mixture was gently refluxed with stirring for four days. At the end of this period, the mixture was cooled to room temperature and filtered off to remove CsCl and the excess unreacted CsCO₃, and the solution was evaporated to dryness using rotary evaporator. The residue was dissolved in CH₂Cl₂ (30 mL) and extracted with H₂O (3 × 20 mL). The organic layer was collected and treated with anhydrous MgSO₄. Upon filtration and evaporating the solvent, the product, which was obtained as viscous yellow oil, was further recrystallized from absolute ethanol with the aid of activated charcoal (1.8 g, 65%). Characterization. Selected IR (cm⁻¹) bands: 1618 (m), 1597 (s), 1568 (m), 1505 (m), 1474 (m), 1434 (m). ESI-MS: m/z = 278.166 [M + H]⁺ and Anal. Calcd for C₁₈H₁₉N₃ = 277.159. ^{1}H NMR (d_6-DMSO, 400 MHz, δ in ppm): δ = 2.24 (3H, s, −CH₃), 2.78, 2.95 (2H, t, CH₂py), 3.80 (2H, s, −CH₂q), 7.17, 7.18, 7.19, 7.25, 7.39, 7.53, 7.68, 7.89, 7.92, 8.21, 8.23, 8.37 (pyridyl and quinolyl protons). ^{13}C NMR: (d_6-DMSO, 100 MHz) δ = 35.4 (CH₃), 42.1, 57.1, 63.7 (CH₂), 120.8, 121.3, 123.1, 126.0, 126.9, 127.7, 128.5, 129.3, 136.1, 146.9, 148.8, 160.1, 160.3 (pyridyl and quinolyl carbons).

Bis(2-methylpyridyl)methylamine (MeDPA). This ligand was synthesized and characterized according to the published procedure.[31]

Synthesis of the Complexes. A general method was used to synthesize all the Cd−azido complexes. To equimolar amounts of Cd(ClO₄)₂·H₂O (Cd(NO₃)₂·4H₂O in the case of complex **1**) and the corresponding amine (0.5 mmol scale) dissolved in methanol (25 mL), two equivalents of NaN₃ (0.065 g, 1.0 mmol) were added. The mixture was heated on a steam-bath to boiling for 10 min, then filtered through Celite and allowed to stand at room temperature. Within 1−4 h (one week in case of complex **1**), the colorless crystals that separated out were collected by filtration, washed with propan-2-ol, Et₂O, and dried in air (overall yield, 50−70%). Single crystals suitable for X-ray structure determination were obtained from dilute solution. In the case of complex **2**, good crystals were obtained upon crystallization from H₂O.

[Cd₂(Meepmqa)₂(μ₁,₃-N₃)₂(N₃)₂] (1). White single crystals were isolated from dilute methanolic solution. Characterization. Selected IR bands: (KBr, cm⁻¹): $\nu_{as}(N_3)$ = 2046 (s), 2036 (s). Anal. Calcd for C₁₇H₁₉CdN₉ (MM = 461.81 g/mol): C, 44.21; H, 4.15; N, 27.30%. Found: C, 43.97; H, 4.08; N, 27.55%.

[Cd₂(MeDPA)₂(μ₁,₁-N₃)₂(N₃)₂] (2). Characterization. Selected IR bands: (KBr, cm⁻¹): $\nu_{as}(N_3)$ = 2044 (vs). Anal. Calcd for

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Table 1. Crystallographic Data and Processing Parameters for Complexes 1−4

compd	1	2	3	4
empirical formula	$C_{36}H_{38}Cd_2N_{18}$	$C_{26}H_{30}Cd_2N_{18}$	$C_8H_{20}CdN_8$	$C_{10}H_{28}Cd_2N_{16}$
formula mass	947.66	819.50	340.73	597.30
system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
a (Å)	9.5324(9)	8.5266(8)	14.5709(14)	14.1759(14)
b (Å)	26.1975(18)	8.7729(9)	15.5050(15)	14.8525(14)
c (Å)	7.8996(6)	11.1630(13)	13.1291(12)	10.5140(11)
α (deg)	90	76.051(17)	90	90
β (deg)	111.624(17)	74.229(18)	114.67(2)	97.91(2)
γ (deg)	90	80.68(2)	90	90
V (Å^3)	1833.9(3)	775.73(17)	2695.4(6)	2192.6(4)
Z	2	1	8	4
μ (mm^{-1})	1.216	1.422	1.615	1.971
D_{calcd} (Mg/m^3)	1.716	1.754	1.679	1.809
crystal size (mm)	0.35 × 0.27 × 0.19	0.40 × 0.32 × 0.26	0.35 × 0.08 × 0.05	0.43 × 0.25 × 0.18
θ max (deg)	26.35	26.30	26.36	26.37
data collected	14477	6091	10522	11443
unique refl./R_{int}	3729/0.0368	3066/0.0156	2754/0.0575	4460/0.0366
parameters/restraints	254/0	209/0	232/0	309/3
goodness-of-fit on F^2	1.166	1.058	1.255	1.080
R_1/wR_2 (all data)	0.0397/0.0872	0.0187/0.0459	0.0660/0.1284	0.0451/0.0992
residual extrema (e/Å^3)	1.92/−0.70	0.53/−0.58	0.88/−1.69	1.06/−0.53

$C_{13}H_{15}CdN_9$ (MM = 409.74 g/mol): C, 38.11; H, 3.69; N, 30.77%. Found: C, 38.13; H, 4.76; N, 30.61%.

[Cd$_2$(Et$_3$en)$_2$($\mu_{1,1}$-N$_3$)$_2$($\mu_{1,3}$-N$_3$)$_2$]$_n$ (3). Characterization. Selected IR bands (KBr, cm^{-1}): ν(N−H) = 3248 (m); ν_{as}(N$_3$) = 2075 (vs), 2056 (vs). Anal. Calcd for $C_8H_{20}CdN_8$ (MM = 340.72 g/mol): C, 28.20; H, 5.92; N, 32.89%. Found: C, 28.51; H, 5.79; N, 32.92%.

[Cd$_4$(Me$_3$en)$_4$($\mu_{1,1}$-N$_3$)$_6$($\mu_{1,3}$-N$_3$)$_2$]$_n$ (4). Characterization. Selected IR bands (KBr, cm^{-1}): ν(N−H) = 3276 (s); ν_{as}(N$_3$) = 2091 (s), 2044 (vs). Anal. Calcd for $C_5H_{14}CdN_8$ (MM = 298.63 g/mol): C, 20.11; H, 4.73; N, 37.52%. Found: C, 20.30; H, 4.79; N, 37.70%.

X-ray Crystal Structure Analysis. The X-ray single-crystal data of compounds **1−4** were collected on a Bruker-AXS SMART CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection, and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo−Kα radiation (λ = 0.71073 Å). Data processing, Lorentz-polarization, and absorption corrections were performed using SAINT, and the SADABS computer programs.[32] The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2, using the SHELXTL[33] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors, and included in the final refinement cycles by using geometrical constraints. Split occupancy factors of 0.5 were applied for atoms of one disordered Et$_3$en and one Me$_3$en ligands in complexes **3** and **4**, respectively. Molecular plots were performed with the Mercury program.[34]

■ RESULTS AND DISCUSSION

Synthesis and IR Spectra of the Complexes 1−4. The reactions of Cd(ClO$_4$)$_2$ or Cd(NO$_3$)$_2$ with tridentate amines derived from quinolyl- or pyridyl methyl amine in MeOH resulted in the formation of the dinuclear complexes [Cd$_2$(Meepmqa)$_2$($\mu_{1,3}$-N$_3$)$_2$(N$_3$)$_2$] (1) and [Cd$_2$(MeDPA)$_2$($\mu_{1,1}$-N$_3$)$_2$(N$_3$)$_2$] (2) with the azido bridges acting as d(EE) and d(EO), respectively. The corresponding reactions with sterically hindered N-substituted poly alkyl ethylenediamine afforded the 1-D polymeric complexes [Cd$_2$(Et$_3$en)$_2$($\mu_{1,1}$-N$_3$)$_2$($\mu_{1,3}$-N$_3$)$_2$]$_n$ (3) and {[Cd$_4$(Me$_3$en)$_4$($\mu_{1,1}$-N$_3$)$_6$($\mu_{1,3}$-N$_3$)$_2$]}$_n$ (4) with different alter-

native bridging azido bonding modes di(EO/EE) and di(EO/EO/EO/EE), respectively (see next X-ray section).

The IR spectra of the complexes display the strong characteristic asymmetric stretching vibration, ν_{as}(N$_3$) of the azide ligand over the range 2040−2090 cm^{-1}. In these four complexes and as in many related bridging Cd(II)-azido complexes, which are collected in Table 2, one or two strong ν_{as}(N$_3$) stretching vibrations were observed where they can be assigned to the presence of different bonding azide modes. Attempts to diagnose the number and locations of the ν_{as}(N$_3$) vibrations to the azide bonding modes reveal the following features:

(1) In general, the Cd−azido complexes have more tendency to form EO-bridging-azide modes than the corresponding EE-bridging modes.

(2) The EO-bridging modes display a single strong sharp band between 2040 and 2060 cm^{-1}. However, this cannot be taken for granted as a criterion for this bonding mode. The complex [Cd$_2$(L^2)$_2$($\mu_{1,1}$-N$_3$)$_4$] where L^2 = trimethylammonio-acetate displayed two strong bands at 2053 and 2071 cm^{-1}.[22b] Most likely, the bridged carboxylato group of L^2 ligand may cause further split of the doubly bridged EO-azide groups.[22b]

(3) Some of the complexes such as in the case of complex **2**, [Cd(3-ampy)($\mu_{1,1}$-N$_3$)$_2$]$_n$, [Cd(8-aminoql)($\mu_{1,1}$-N$_3$)$_2$]$_n$, and [Cd(3,5-daba)($\mu_{1,1}$-N$_3$)$_2$]$_n$, which exhibit EO bonding modes, have their bands very close to ν_{as}(N$_3$) reported for the ionic azide in KN$_3$ (2039 cm^{-1}).[6f,19,21b,35]

(4) Structurally characterized compounds containing EE- or mixed EE/EO-bridged azides (Table 2) reveal the presence of two strong ν_{as}(N$_3$) stretching vibrations. However, this is not the case in the two polymeric species [Cd(3-acpy)$_2$($\mu_{1,1}$-N$_3$)$_2$($\mu_{1,3}$-N$_3$)]$_n$ and [Cd$_2$(N$_2$H$_4$)($\mu_{1,1}$-N$_3$)$_2$($\mu_{1,3}$-N$_3$)(N$_3$)]$_n$ where a single band was detected (Table 2).[16,26b]

Thus, from this discussion it is obvious that the ν_{as}(N$_3$) of the azido group in azido−Cd(II) could help in predicting the bonding coordination mode of the bridged azide, but it cannot be used as a diagnostic tool to elucidate for certainty the

Table 2. Asymmetric Stretching Frequency, $\nu_{as}(N_3)$, of the Azide Group in Some Cd(II)−Azido Complexes

complex[a]	$\nu_{as}(N_3)$	ref
$[Cd_2(MeDPA)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**2**)	2044	this work
$[Cd(bpfd)(\mu_{1,1}\text{-}N_3)(N_3)]\cdot 3H_2O$[b]	2056	18c
$[Cd_5(bpp)_6(\mu_{1,1}\text{-}N_3)_6(\mu_2\text{-}Cl_2)Cl_2]_n$[c]	2056	26
$[Cd(3\text{-}ampy)(\mu_{1,1}\text{-}N_3)_2]_n$[d]	2040	21b
$[Cd(8\text{-}aminoql)(\mu_{1,1}\text{-}N_3)_2]_n$[e]	2044	19
$[Cd_4(dafone)_4Cl_2(\mu_{1,1}\text{-}N_3)_4(\mu_{1,1,1}\text{-}N_3)_2]$[f]	2059	28a
$[Cd_4(dafone)_4(N_3)_2(\mu_{1,1}\text{-}N_3)_4(\mu_{1,1,1}\text{-}N_3)_2]$[f]	2058	28a
$[Cd_2(L^1)_2(\mu_{1,1}\text{-}N_3)_4]$[g]	2058	18a
$[Cd(3,5\text{-}daba)(\mu_{1,1}\text{-}N_3)_2]_n$[h]	2042	6f
$[Cd(abpt)(\mu_{1,1}\text{-}N_3)_2]_n$[i]	2059	22a
$[Cd_2(L^2)_2(\mu_{1,1}\text{-}N_3)_4]$[j]	2053, 2071	22b
$[Cd_2(Meepmqa)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$ (**1**)	2036, 2046	this work
$[Cd(Quz)_2(\mu_{1,3}\text{-}N_3)_2]_n$[k]	2036, 2068	23b
$[Cd_2(dmpz)_2(\mu_{1,3}\text{-}N_3)_4]_n$[l]	2053, 2065	23b
$[Cd(bdmpzm)(\mu_{1,1}\text{-}N_3)_4(\mu_{1,3}\text{-}N_3)_2]_n$[m]	2060, 2078	27
$[Cd_2(Et_3en)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)_2]_n$ (**3**)	2056, 2075	this work
$[Cd_4(Me_3en)_4(\mu_{1,1}\text{-}N_3)_6(\mu_{1,3}\text{-}N_3)_2]_n$ (**4**)	2044, 2091	this work
$[Cd_2(3\text{-}abpt)(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)_2]_n$[n]	2053, 2092	26a
$[Cd_2(N_2H_4)(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)(N_3)]_n$	2041	26b
$[Cd(4\text{-}Etpy)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)]_n$[o]	2033, 2085	16
$[Cd(4\text{-}OHMepy)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)]_n$[p]	2037, 2060	16
$[Cd(3\text{-}acpy)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)]_n$[q]	2037	16

[a]Ligand abbreviations. [b]bpfd = N,N′-(bis(pyridine-2-yl)formylidene)-ethane-1,2-diamine. [c]bpp = 1,3-bis(4-pyridyl)propane. [d]3-ampy = 3-aminopyridine}. [e]aminoql = 8-aminoquinoline. [f]dafone = 4,5-diazafluoren-9-one. [g]L^1 = N-(4,6-dimethylpyrimidine-2-yl)-N-(1-pyridin-2-yl-ethylidin)-hydrazine. [h]3,5-daba = 4-aminobenzoate. [i]abpt = 4-amino-3,5bis(pyridin-2-yl)-1,2,4-triazole. [j]L^2 = trimethylammonio-acetate. [k]Quz = quinolone. [l]dmpz = 2,5-dimethyl-pyrazine. [m]bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane). [n]abpt = 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole. [o]4-Etpy = 4-ethylpyridine. [p]4-HOMepy = 4-hydroxymethylpyridine; [q]3-acpy = 3-acetylpyridine.

bonding mode of the azide groups in these complexes. Most probably this is attributed to the strong influence of the ligand skeletal structure and the environment around the Cd(II) centers, which may result in the split of the $\nu_{as}(N_3)$ and/or leading to broadening of the band.

Structure Description of the Complexes 1−4. The structure of $[Cd_2(Meepmqa)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$ (**1**) consists with the neutral centrosymmetric dinuclear complexes $[Cd_2(Meepmqa)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$. The atom numbering scheme is presented in Figure 1, and selected bond parameters are summarized in Table 3. Cd(1) is octahedrally coordinated by three N donor atoms of the Meepmqa ligand in a *mer*-conformation, N(11) and N(13) of EE-bridging azido groups, and N(21) of a terminal azido group. The Cd−N bond lengths range from 2.276(3) to 2.568(3) Å. The Cd(1)···Cd(1′) [(′): −x,−y,−z] distance is 5.9750(7) Å, and the shortest interdimer metal−metal separation is 7.8996(8) Å. The bond parameters for the azido ligands are N(11)−Cd(1)−N(13) = 82.89(11)°, Cd(1)−N(11)−N(12′) = 149.0(3)°, Cd(1)−N(13)−N(12) = 124.0(3)°, and Cd(1)−N(21)−N(22) = 124.8(3)°. The azido groups have N−N−N bond angles of 176.4(4)° and 178.0(4)° and are almost symmetric [mean Δd(N−N) = 0.020(5) Å]. The two EE azido bridges connect the two Cd(II) centers to form a centrosymmetric eight-membered Cd(1)−$(\mu_{1,3}\text{-}N_3)_2$−Cd(1′) ring. This eight-membered ring has a distortion from the planar to a chair-like arrangement with a δ-angle of 5.8° [δ-angle is defined as the dihedral angle between the mean plane
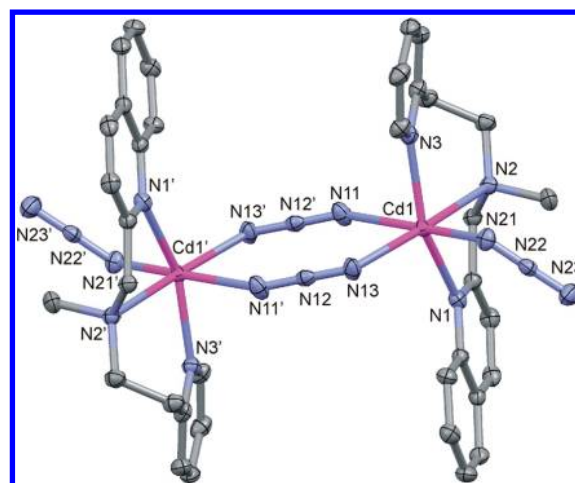
Figure 1. Perspective view of dinuclear complex of **1**.

of the six N atoms of the di-EE bridge and the N(11)−Cd(1)−N(13) plane].[36] The Cd(1)−N(11)···N(13′)−Cd(1′) torsion angle is 14.0°. Along the monoclinic a-axis, the dinuclear complexes are connected to a supramolecular 1D system via π−π stacking interactions of the aromatic rings of adjacent Meepmqa ligands. The separations of the centers of gravities of their six-membered heterocyclic pyridyl- and quinolyl-rings range from 3.510(2) to 3.966(2) Å.

A perspective view of the neutral centrosymmetric dinuclear complex $[Cd_2(MeDPA)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**2**) together with the atom numbering scheme are given in Figure 2, and selected bond parameters are collected in Table 3. Cd(1) is octahedrally coordinated by three N donor atoms of the MeDPA ligand in a *mer*-conformation, N(11) and N(11′) [(′): 1 − x,−y,−z] of EO-bridging azido groups, which form the common edge within the dinuclear units, and N(21) of a terminal azido group. The Cd−N bond lengths are in the range from 2.2601(17) to 2.4433(16) Å. The Cd(1)···Cd(1′) distance is 3.6842(5) Å, and the shortest interdimer metal−metal separation is 7.7367(9) Å (Figure S2, Supporting Information). The bond parameters for the azido ligands are Cd(1)−N(11)−Cd(1′) = 104.31(6)°, N(11)−Cd(1)−N(11′) = 75.69(6)°, N(11′)···N(11)−N(12) = 154.6(2), Cd(1)−N(11)−N(12) = 124.33(13)°, Cd(1′)−N(11)−N(12) = 122.99(13), and Cd(1)−N(21)−N(22) = 117.08(13)°. The azide groups have N−N−N bond angles of 178.6(2)° and 177.69(19)° and are asymmetric [Δd(N−N) = 0.048(3) Å].

The structure of $[Cd_2(Et_3en)_2(\mu_{1,1}\text{-}N_3)_2(\mu_{1,3}\text{-}N_3)_2]_n$ (**3**) (Figure 3, and selected bond parameters are collected in Table 3) consists of octahedrally coordinated cadmium atoms in which the coordination sites are occupied by two N atoms of the disordered Et₃en ligand in cis arrangement and four azido ligands from double bridges between neighboring cadmium atoms. The Cd−N bond lengths are in the range from 2.300(7) to 2.403(6) Å. The azido groups in the double bridges are alternatively in the EE and EO modes generating an alternating chain oriented along the c-axis of the monoclinic unit cell. The end-on azido bridges show asymmetric N−N distances of 1.217(8)/1.144(9) Å, whereas the end-to-end bridges are more symmetric: 1.164(8)/1.140(8) Å. The bond parameters within the $Cd_2(\mu_{1,3}\text{-}N_3)_2$ ring are N(21)−Cd(1)−N(23′) = 91.2(2)°, Cd(1)−N(21)−N(22) = 126.0(6)°, and Cd(1)−N(23′)−N(22′) = 131.8(5)°; torsion angle, Cd(1)−N(21)···N(23)−Cd(1′) = −23.0° [(′): 1 − x,y,−z + 1/2]. This eight-membered

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1−4

compound 1[a]			
Cd(1)−N(11)	2.568(3)	Cd(1)−N(1)	2.332(3)
Cd(1)−N(13)	2.296(3)	Cd(1)−N(2)	2.466(3)
Cd(1)−N(21)	2.276(3)	Cd(1)−N(3)	2.306(3)
N(11)−N(12′)	1.168(5)	N(12)−N(13)	1.185(4)
N(21)−N(22)	1.162(2)	N(22)−N(23)	1.166(5)
N(11)−Cd(1)−N(21)	172.95(11)	N(1)−Cd(1)−N(3)	155.10(11)
N(13)−Cd(1)−N(2)	171.69(11)		
compound 2[b]			
Cd(1)−N(11)	2.3033(17)	Cd(1)−N(1)	2.3880(16)
Cd(1)−N(11′)	2.3618(17)	Cd(1)−N(2)	2.4433(16)
Cd(1)−N(21)	2.2601(17)	Cd(1)−N(3)	1.3294(16)
N(11)−N(12)	1.210(2)	N(12)−N(13)	1.147(3)
N(21)−N(22)	1.197(2)	N(22)−N(23)	1.165(2)
N(11′)−Cd(1)−N(21)	106.67(6)	N(11)−Cd(1)−N(3)	157.58(6)
N(11′)−Cd(1)−N(1)	157.34(6)	N(21)−Cd(1)−N(2)	148.37(6)
compound 3[c]			
Cd(1)−N(11)	2.322(6)	Cd(1)−N(1)	2.322(6)
Cd(1)−N(11″)	2.359(6)	Cd(1)−N(2)	2.403(6)
Cd(1)−N(21)	2.300(7)	Cd(1)-N(23′)	2.397(7)
N(11)−N(12)	1.217(8)	N(12)−N(13)	1.144(9)
N(21)−N(22)	1.164(8)	N(22)−N(23)	1.140(8)
N(11″)−Cd(1)−N(23′)	166.6(2)	N(21)−Cd(1)−N(1)	174.4(3)
N(11)−Cd(1)−N(2)	169.7(2)		
compound 4[d]			
Cd(1)−N(11)	2.361(4)	Cd(1)−N(1)	2.349(4)
Cd(1)−N(21)	2.301(4)	Cd(1)−N(2)	2.364(5)
Cd(1)−N(31)	2.318(5)	Cd(1)−N(33″)	2.377(5)
Cd(2)−N(11)	2.348(4)	Cd(2)−N(3)	2.418(11)
Cd(2)−N(21)	2.346(4)	Cd(2)−N(4)	2.38(2)
Cd(2)−N(41)	2.373(5)	Cd(2)−N(30)	2.310(13)
Cd(2)-N(41′)	2.370(4)	Cd(2)−N(40)	2.37(2)
N(11)−N(12)	1.208(6)	N(12)−N(13)	1.148(6)
N(21)−N(22)	1.188(6)	N(22)−N(23)	1.143(8)
N(31)−N(32)	1.155(7)	N(32)−N(33)	1.124(6)
N(41)−N(42)	1.196(6)	N(42)−N(43)	1.147(7)
N(31)−Cd(1)−N(1)	168.3(2)	N(21)−Cd(1)−N(41)	164.90(16)
N(21)−Cd(1)−N(2)	170.65(17)	N(41′)−Cd(1)−N(4)	175.6(4)
N(11)−Cd(1)−N(33′)	166.57(19)	N(11)−Cd(1)−N(3)	161.0(3)
Cd(1)−N(11)−Cd(2)	100.85(16)	Cd(1)−N(21)−Cd(2)	102.73(16)
Cd(2′)-N(41)−Cd(2)	100.89(17)		

[a]('): −x,−y,−z. [b]('): 1 − x,−y,−z. [c]('): 1 − x,y,−z + 1/2. (″): 1 − x,−y.−z. [d]('): −x,2 − y,1 − z. (″): 1 − x,2 − y,1 − z.
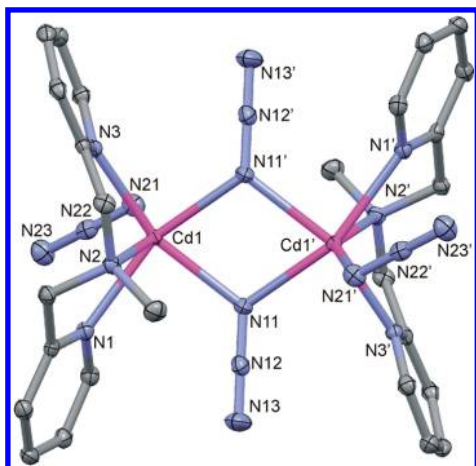

Figure 2. Perspective view of dinuclear complex of **2**.

ring $Cd_2(\mu_{1,3}\text{-}N_3)_2$ shows a distortion from the planar to a boat-like conformation with a δ-angle of 16.3°, whereas the four-membered $Cd_2(\mu_{1,1}\text{-}N_3)_2$ ring is planar. The intrachain Cd···Cd distance within the four-membered ring is 3.6300(8) Å, and that within the eight-membered ring is 5.4438(9) Å, whereas the interchain metal···metal separation is 7.3489(10) Å. The bond parameters of the di-EO azido bridge are N(11)−Cd(1)−N(11″) = 78.3(2)°, Cd(1)−N(11)−N(12) = 121.0(5)°, Cd(1″)−N(11)−N(12) = 134.0(5)°, Cd(1)−N(11)−Cd(1″) = 101.7(2)°, and N(11″)···N(11)−N(12) = 163.5(9)° [(″): 1 − x,−y,−z]. The azido groups have N−N−N bond angles of 178.5(9)° and 174.6(8)°.

The asymmetric unit of the monoclinic unit cell of $[Cd_4(Me_3en)_4(\mu_{1,1}\text{-}N_3)_6(\mu_{1,3}\text{-}N_3)_2]_n$ (**4**) contains two crystallographically independent Cd(II) centers, one ordered and one disordered Me₃en ligand and four azido groups. A perspective view of a section of the neutral polymeric $[Cd_2(Me_3en)_4(N_3)_4]_n$ chain of **4** together with the atom numbering scheme are given
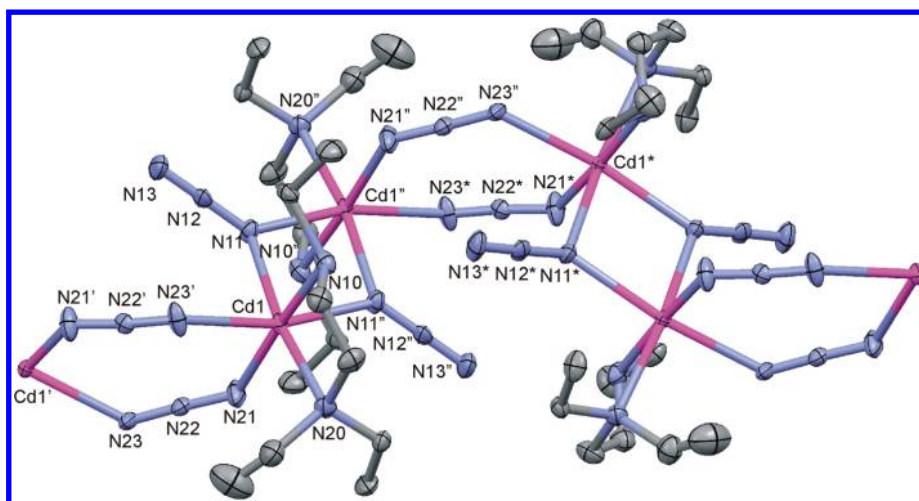
Figure 3. Perspective view of a section of the 1D system of **3**. Only one orientation of the disordered Et₃en ligand is given for clarity.

in Figure 4, and selected bond parameters are collected in Table 3. Both Cd(II) centers are octahedrally coordinated by
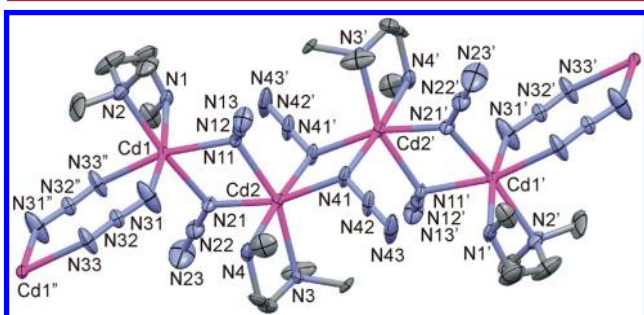

Figure 4. Perspective view of a section of the 1D system of **4**. Only one orientation of the disordered Me₃en ligand is given for clarity.

two N donor atoms of the Me₃en ligands in cis arrangement and four N atoms of azido bridges. The Cd−N(N₃) bond distances are in the range from 2.301(4) to 2.377(5) Å, and the

Cd−N(Me₃en) bond distances vary from 2.310(13) to 2.418(11) Å. The azido bridges show an alternating Cd(1)−(EO)₂−Cd(2)−(EO)₂−Cd(2′)−(EO)₂−Cd((1′)−(EE)₂ sequence [(′) −x,2 − y,1 − z] giving rise to the 1D system, which is oriented along the a-axis of the monoclinic unit cell. The centrosymmetric Cd(1)−(EE)₂−Cd(1″) azido bridge has a chair-like arrangement with the δ-angle of 7.0°. The Cd(1)⋯Cd(1″) [(″) 1 − x,2 − y,1 − z] intra-chain distance is 5.5955(7) Å, and the Cd(1)−N(31)⋯N(33)−Cd(1″) torsion angle is 14.1°. The four-membered Cd₂N₂ rings formed by the three consecutive di-EO azido bridges have intra-chain metal⋯metal distances of 3.6295(6) and 3.6566(7) Å and the Cd−N−Cd bond angles are in the range from 100.85(16) to 102.73(16)°. The angles N(41′⋯N(41)−N(42), N(21)⋯N(11)−N(12), and N(11)⋯N(21)−N(22) are 139.8(7), 150.3(7) and 175.0(7)°, respectively. The azido bridges have Cd−N−N and N−N−N bond angles varying from 117.0(4) to 135.1(4) and from 175.0(6) to 179.3(8)°, respectively, and are asymmetric [Δd(N−N) = 0.036(7) Å]. As a consequence of the cis arrangement of the Me₃en ligands, the back-bone of the
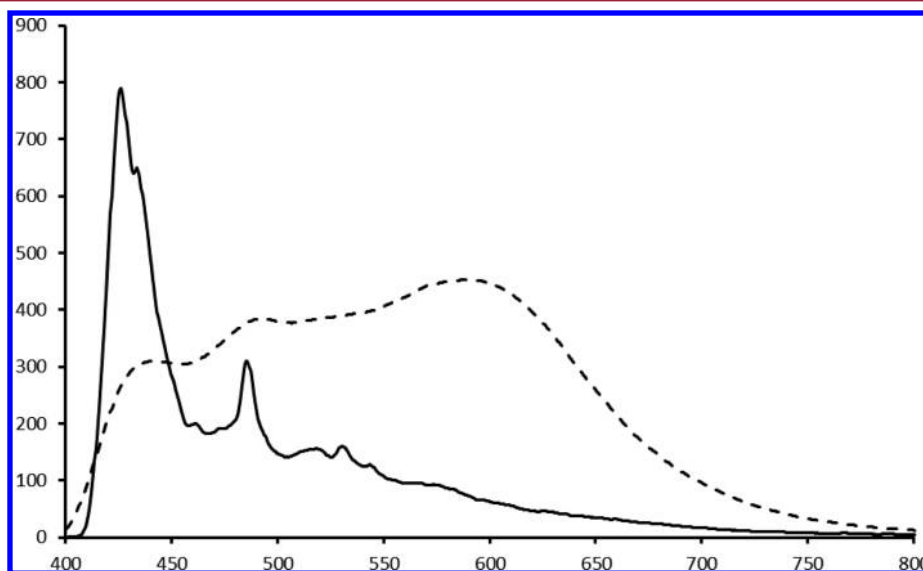

Figure 5. Fluorescence emission [intensity (arbitrary units) vs wavelength (in nm)] of complex **1** and its corresponding Meepqa ligand. The solid line represents the Cd(II) azido complex, **1**, and the broken line is for the free ligand.

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1D system is corrugated with Cd···Cd···Cd angles from 115.8 to 121.5°. Intra-chain hydrogen bonds of type N—H···N are formed from N(1) and N(4) donors of the amine ligands to noncoordinated acceptor N-azido atoms N(43″) and N(31), with N···N separations of 3.048(7) and 3.31(2) Å, respectively. The azido bridging sequence $[-(EO)_2-(EO)_2-(EO)_2-(EE)_2-]_n$ has been observed in $[Mn(phen)(N_3)_2]_n$ (phen = o-phenathroline)[37] and $[Cd(4-OHMepy)_2(N_3)_2)]_n$ (4-OHMepy = 4-hydroxymethylpyridine).[16] In the latter Cd(II) compound, the 4-OHMepy ligands are in trans arrangement.

Emission Behavior of Cd(II)—Azido Complexes (1—4). The ligands MeDPA, Et$_3$en, and Me$_3$en and their corresponding Cd(II)—azido complexes, **2—4**, showed negligible to very weak emission intensities, in contrast to the ligand Meepmqa and its complex $[Cd_2(Meepmqa)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$ (**1**) showed strong fluorescence enhancement; therefore, our focus on this section was on complex **1**. The emission spectrum of complex **1** was recorded at room temperature on excitation at 366 and 240 nm, respectively. As shown in Figure 5, the free ligand Meepmqa exhibits three fluorescence peaks at 442, 493, and 589 nm with the latter peak having the strongest intensity. Upon complexation, a more complex emission spectrum was obtained with a distinct enhanced fluorescence intensity at 425 nm; also, the peak positions showed a dramatic blue shift. In general, the enhancement of the emission intensities of metal complexes may be due to the metal ligand chelation[27,38−40] or the increase in conformational rigidity of the ligands upon coordination.[38,39] This phenomenon has been reported in d^{10} metal complexes, especially those containing fused ring structures with nitrogen heterocycles.[19,40] The revealed enhanced fluorescence intensity observed in complex **1** may be attributed to the chelation enhanced fluorescence (CHEF) as a result of the improved overlap in the Cd—N bond in the five-membered chelate ring containing the quinolyl moiety. The better the chelating ring size for accommodating the metal ion, the better the overlap in the Cd—N quinolyl bond, thereby reducing the nonradiative decay within the intraligand ($n−\pi^*$) excited state, and the greater the CHEF effect.

However, it should be mentioned that enhancement of emission fluorescence through metal chelation is not a very common phenomenon but instead quenching of fluorescence intensities is observed in most cases.[27,39−41] This may result from the poor overlap of the orbitals of the N-donors in the chelate ring where the poorer overlap makes the electron pairs in higher energy orbitals more readily available for quenching the fluorescence.[38,40] The enhancement of fluorescence phenomenon through complexation is now attracting more attention because of the possible use of these complexes as photochemical devices.[42]

CONCLUSIONS

Sterically hindered two NNN donor pyridyl based ligands (Meepmqa and MeDPA), and two N,N,N-trialkyl-ethylenediamine (Et$_3$en and Me$_3$en) have been used to synthesize a new series of bridged-azido di- and polynuclear Cd(II) complexes. With Meepmqa and MeDPA ligands, dinuclear doubly bridged-azido $\mu_{1,3}$-N$_3$ (EE) and $\mu_{1,1}$-N$_3$ (EO) were isolated, respectively. The corresponding reactions with Et$_3$en and Me$_3$en ligands afforded interesting polynuclear complexes with different alternate azido bridges Cd—(EE)$_2$—Cd—(EO)$_2$—Cd—(EE)$_2$—Cd—(EO)$_2$— and Cd—(EO)$_2$—Cd—(EO)$_2$—Cd—(EO)$_2$—Cd—(EE)$_2$— sequences, respectively. IR spectral analyses for the stretching frequency of $\nu_{as}(N_3)$ of the azido group in the synthesized complexes and in related azido—Cd(II) complexes revealed that $\nu_{as}(N_3)$ cannot be used as a diagnostic tool to elucidate for certainty the bonding mode of the coordinated azide groups in these complexes. The Cd complex **1** shows a strong chelation induced enhanced fluorescence compared to the free ligand Meepmqa from which the complex was derived. The involvement of the nonbonding lone pair of electrons of the N-donor of the quinolyl group in strong bond formation with Cd^{2+} ion causes the suppression of the $n−\pi^*$ transitions and the nonflexibility of the corresponding five-membered chelate ring. The strength of the Cd—N quinolyl bond and the inactive nonradiative channels may be the reason for the CHEF in complex **1**.

ASSOCIATED CONTENT

Supporting Information

CIF files of compounds 1—4, and the corresponding packing plots for the crystal structures are presented in Figures S1—S4, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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