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Magnetic properties of 1 : 4 complexes of $CoCl_2$ and pyridines carrying carbenes ($S_0 = 4/2$, 6/2, and 8/2) in diluted frozen solution; influence of carbene multiplicity on heterospin single-molecule magnets[†]

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The microcrystalline sample of a parent complex, $[CoCl_2(py)_4]$, showed a single-molecule magnet (SMM) behavior with an effective activation barrier, U_{eff}/k_B , of 16 K for reversal of the magnetism in the presence of a dc field of 3 kOe. Pyridine ligands having 2–4 diazo moieties, **DYpy**; **Y** = **2**, **31**, **3b**, and **4**, were prepared and confirmed to be quintet, septet, septet, and nonet in the ground state, respectively, after irradiation. The 1 : 4 complexes, $CoCl_2(DYpy)_4$; **Y** = **2**, **31**, **3b**, and **4** in frozen solutions after irradiation showed the magnetic behaviors of SMMs with total spin multiplicity, $S_{total} = 17/2$, 25/2, 25/2, and 33/2, respectively. Hysteresis loops depending on the temperature were observed and the values of coercive force, H_c , at 1.9 K were 12, 8.4, 11, and 8.1 kOe for $CoCl_2(CYpy)_4$; **Y** = **2**, **31**, **3b**, and **4**, respectively. In dynamic magnetic susceptibility experiments, ac magnetic susceptibility data obeyed the Arrhenius law to give U_{eff}/k_B values of 94, 92, 93, and 87 K for $CoCl_2(CYpy)_4$; **Y** = **2**, **31**, **3b**, and **4**, respectively, while the relaxation times for $CoCl_2(CYpy)_4$; **Y** = **2** and **31**, obtained by dc magnetization decay in the range of 3.5-1.9 K slightly deviated downward from Arrhenius plots on cooling. The dynamic magnetic behaviors for $CoCl_2(CYpy)_4$ including $[CoCl_2(py)_4]$ and $CoCl_2(C1py)_4$ suggested that the generated carbenes interacted with the cobalt ion to increase the relaxation time, τ_q , due to the spin quantum tunneling magnetization, which became larger with increasing S_{total} of the complex.

Introduction

One of the striking characteristics of the single-molecule magnets $(SMMs)^{1-4}$ exhibiting a slow magnetic relaxation is the size as a magnet. Because in SMMs, an individual molecule functions as a magnet, the size of the magnet depends on the molecular size. Furthermore, an important physical property of SMMs is the quantum tunneling of magnetization $(QTM)^2$ observed at extremely low temperature. From these unique magnetic properties, SMMs are expected to allow the development of new magnetic materials. To date, many complexes and clusters containing various kinds of $3d^3$ and $4f^4$ metal ions have been reported as SMM. At the present stage, the construction of a SMM with a high activation barrier for the reversal of

E-mail: koga@fc.phar.kyushu-u.ac.jp; Fax: +81-92-642-6590; Tel: +81-92-642-6590 magnetism presents an interesting challenge in the field of the molecule-based magnet. For the construction of SMM, we have been using a heterospin system^{5,6} consisting of the 3d spins of the metal ions and the 2p organic spins. In the heterospin system, the combination of the anisotropic high-spin cobalt(II) ion and aminoxyl- and carbene-pyridine ligands (4NOpy and C1py, respectively) were selected and those complexes successfully provided heterospin SMM with relatively large effective activation barriers, $U_{eff}/k_{\rm B}$. In the simple 1:4 cobalt(II) complexes, $[Co(X)_2(Y)_4]$; X = counter anion and Y = 4NOpy and C1py, the magnetic properties of heterospin SMMs were found to depend on the axial ligand, X, and the equatorial one, Y. The complexes, $CoX_2(4NOpy)_4^{5a}$ and $CoX_2(C1py)_4^{5b}$ behaved as SMMs in frozen solution; the $U_{\rm eff}/k_{\rm B}$ values were 50, 31, and 20 K for X = NCO⁻, NCS⁻, and Br⁻, respectively, in $CoX_2(4NOpy)_4$ and 130, 89, and 91 K for X = NCO⁻, NCS⁻, and Cl^- , respectively, in $CoX_2(C1py)_4$.

In order to understand the heterospin SMM properties, this time, the influence of the spin multiplicity of carbene spin, S_0 , at the equatorial ligands on the SMM properties was investigated. In the cobalt-carbene complex, it is possible to vary the total *S* value, S_{total} , of the SMM complex systematically by altering the number of carbenes. Carbene, being a divalent carbon, is a reactive intermediate in fundamental organic chemistry, and especially diphenylcarbene, having a triplet ground state, has

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[†]Electronic supplementary information (ESI) available: UV-Vis spectra changes of **D2bpy** in solution on photolysis at 10 K (S1), *M vs.* irradiation time plot for **D2py** and CoCl₂(**D2py**)₄ (S2), data of slow relaxation of magnetization for [CoCl₂(**py**)₄] (S3), and plots of hysteresis loops (S4), $\chi'_{mol} T vs. T$ (S5), dc decay (S6), and $\tau vs. T^{-1}$ (S7) for 1 : 4 mixtures of CoCl₂ and **CYpy**; **Y** = **2**, **31**, **3b**, and **4**. See DOI: 10.1039/c2dt31288c

been used as a building block for high-spin organic molecules. Based on polycarbene studies,⁷ the diazo-pyridine derivatives, **D2py**, **D3py**, and **D4py**, connecting two, three, and four diazo moieties with ferromagnetic *m*-phenylene linkers, were designed as precursors of high-spin carbene. The carbene centers generated by photolysis of **D2py**, **D3py**, and **D4py** interact ferromagnetically to form high-spin carbenes, **C2py**, **C3py**, and **C4py**, with $S_0 = 4/2$, 6/2, and 8/2, respectively. Since the carbene at the 4-position of the pyridine ring ferromagnetically interacts with the high-spin cobalt(II) ion with the effective spin, $S_{\text{eff}} = 1/2$,⁸ the 1 : 4 complexes $CoX_2(CYpy)_4$, where Y = 1, **2**, **31**, **3b**, and **4** are expected to produce the high-spin ground state with $S_{\text{total}} = 9/2$, 17/2, 25/2, 25/2, and 33/2, respectively.



In this study, the chloride ion was selected as the axial ligand and a frozen solution condition was used for the effective photolysis of diazo moieties in the complex. The ac and dc magnetic susceptibility measurements for the 1 : 4 complexes of CoCl₂-(**DYpy**)₄; Y = 2, 3l, 3b, and 4, in frozen solution after irradiation were carried out. In addition, the magnetic property of the parent 1 : 4 complex, $[CoCl_2(py)_4]$, having no diazo unit was also investigated in the microcrystalline state.

Results and discussion

Preparations of di-, tri-, tetradiazo-pyridine derivatives and their cobalt(11) complexes

Based on the studies of the high-spin polycarbenes,⁷ mono-, di-, tri-, and tetracarbene-monopyridine derivatives were designed, in which a pyridine and carbene centers served as binding ligands for the metal ion and organic spin source, respectively. Each carbene center was connected with *m*-phenylene ferromagnetic coupler and the carbene center was located at the 4-position of the pyridine ring. The diazo-pyridine derivatives, DYpy, which were precursors of corresponding high-spin carbenes, were prepared by the modified procedure reported previously.^{6f,7} Two isomeric tridiazo-pyridine derivatives, D3bpy and D3lpy, which had branched and linear structures, respectively, were designed and prepared. In the branched one, tert-butyl groups were introduced at the *p*-position of the benzene ring to increase the solubility in organic solvent after the complexation with cobalt ion. Preparations of **DYpy**; Y = 2, 31, 3b, and 4, are summarized in Scheme 1.

The lithiation of starting bromo derivatives, 1 and 2, which were prepared by the procedure reported previously, 5g,7,9 with *n*-butyllithium was followed by the reaction with 4-formylpyridine to afford carbinol 4 and 5. Grignard reagent prepared from 3,3'-bromodiphenylmethane 3 and magnesium reacted with

3-formyldiphenylmethane to give a carbinol 6. After reduction to methylene with trimethylsililchloride-sodium hydride,¹⁰ bromide 7 was lithiated with *n*-butyllithium followed by the reaction with 4-formylpyridine to afford 8. Hydroxy derivatives, 4, 5, and 8, were oxidized with sodium perchromate(vi) to the corresponding ketones, **OYpy**; Y = 2, 3l, and 4. The dilithiation of 1,3,5-tribromobenzene with tert-butyllithium followed by the reaction with 4-tert-butylbenzaldehyde gave a mixture of dihydroxy derivative 9 containing a monoketo-monohydroxy derivative. A mixture was reduced with sodium borohydride to dihydroxy derivative 9, and then by the reaction with trimethylsililchloride-sodium hydride to bromide 10. Similarly, bromide 10 was lithiated and was reacted with 4-formylpyridine to afford 11. Hydroxy derivative 11 was oxidized stepwise; first, with manganese(IV) dioxide to monoketone 12, and after the purification, secondly oxidized with sodium perchromate(VI) to triketone **O3bpv**. The direct oxidation with sodium perchromate(vi) from 11 to triketone gave a poor yield. Bisdiazo-, tridiazo-, and tetradiazo-pyridine ligands, DYpy; Y = 2, 3l, 3b, and 4, were prepared from the corresponding ketone derivatives by a standard procedure;^{6f,7} hydrazone formation, followed by oxidation with freshly prepared active manganese dioxide. Diazo derivatives **DYpy** were purified by column chromatography (Al_2O_3) and then by recrystallization from Et₂O, Et₂O-CH₂Cl₂, and Et₂O, to afford red single crystals for Y = 1, 2, and 3b, and reddish powders for Y = 3I and 4, which were stable in the dark.

In this study, for the investigation of the equatorial ligand effect, the chloride ion was used at the axial ligand. The 1:4 cobalt(II) complexes, $CoCl_2(DYpy)_4$; **Y** = 1, 2, 3l, 3b, and 4, were prepared by mixing the solution of $CoCl_2$ in EtOH with the solution of **DYpy** in CH₂Cl₂ at 1 to 4 ratios. Attempts to obtain the single crystals of $[CoCl_2(DYpy)_4]$ were carried out under various conditions. However, all attempts gave the 1:4 complexes as red powders. The crystal of the parent 1:4 complexes, $[CoCl_2(py)_4]$, which was an elongate octahedron in the molecular structure, was obtained by the procedure reported previously.^{5g}

Measurements of Vis-NIR spectra

(A) DYpy; Y = 1, 2, 3l, 3b and 4. UV-Vis spectra for diazopyridine, **D1py** in MTHF solution (1 mM) at room temperature showed two absorptions at 283 and 500 ($\varepsilon = 1.2 \times 10^2$) nm. The latter one is characteristic of the $n-\pi^*$ transition due to the diazo group. When the irradiation ($\lambda = 514$ nm) started at 10 K, this absorption decreased and two new absorptions appeared at 508 and 471 nm due to π - π * transition. Similarly, diazo-pyridines, **D2py**, **D3bpy**, **D3lpy**, and **D4py** had absorptions at 508 ($\varepsilon = 2.1$ $\times 10^{2}$), 512 (3.1 $\times 10^{2}$), 510 (3.6 $\times 10^{2}$), and 510 (4.2 $\times 10^{2}$) nm due to the $n-\pi^*$ transition and their absorption coefficiencies, (ε , were proportional to the number of diazo moieties). After irradiation under similar conditions, new broad absorptions were observed at 411 and 476 nm for C2py, 406 and 471 nm for C3lpy, 411 and 476 nm for C3bpy, and 420 and 472 nm for C4py. The spectra after irradiation closely resembled that for diphenylcarbene (465 nm) reported previously.^{5g,6f} All new absorptions observed after irradiation disappeared at temperatures higher than 60 K. The absorption change for D2py on photolysis is shown in Fig. S1.[†]



i) n-BuLi/dist.Et₂O, ii) 4-Formylpyridine, iii) Mg/dist.Et₂O, 3-Formyldiphenylmethane, iv) TMS-CI, Nal/CH₃CN, *n*-Hexane, v)Na₂Cr₂O₇•2H₂O/AcOH, vi) NH₂NH₂, NH₂NH₂• HCl/DMSO, vii) MnO₂/CH₂Cl₂,

Scheme 1 Preparation routes for DYpy; Y = 2, 3l, 3b, and 4.

(B) $CoCl_2(DYpy)_4$; Y = 1, 2, 3b, 3l, and 4. In order to investigate the coordination structure of the complexes formed in frozen solutions, Vis-NIR spectra of 1:4 mixtures (5 mM) of CoCl₂ and **DYpy** in MTHF were measured in the temperature range 280-175 K. The spectra of the 1:4 mixtures at room temperature showed two sets of absorptions at 600-700 and \sim 1000 nm and at \sim 500 nm. The latter absorption maximum was not clear due to overlapping with that (510 nm) due to $n-\pi^*$ transition of diazo moieties of DXpy. The former and the latter absorptions are characteristic of the d-d transitions of the cobalt(II) ion in tetrahedral and octahedral structure, respectively.¹¹ On cooling to 200 K, absorptions for the former gradually decreased and the latter at ~500 nm increased (Fig. 1a). At 200 K, the former absorptions disappeared completely. The observed spectral change indicated that the tetrahedral and octahedral species were equilibrated with the former and the latter dominant at room temperature and temperature below 200 K, respectively.5b The observed thermal spectral changes on cooling suggested that the 1:4 mixture in frozen solution can be safely considered to be octahedral as observed in X-ray crystallography.^{5b,12} The solution of the sample was cooled down to 10 K and was irradiated by argon laser ($\lambda = 514$ nm). After irradiation for 2 h, a new absorption at 400-600 nm appeared at the expense of the one at \sim 500 nm for diazo moieties of **DYpy**. This new absorption observed after irradiation was characteristic for the carbene and disappeared after annealing at 70 K.

The changes of Vis spectra for the sample of a 1:4 mixture of CoCl₂ and **D2py** in MTHF solution on cooling from 280 to 175 K and on photolysis at 10 K are shown in Fig. 1(a) and 1(b), respectively. The other combinations of CoCl₂ and **DYpy** showed similar spectral changes on cooling and on photolysis at 10 K.

Magnetic properties

Photolysis of the frozen solution samples. Photolysis of the frozen solution samples were performed in SQUID apparatus by the light from an argon laser (50 mW, $\lambda = 514$ nm) through the optical fiber and were followed by magnetization (M_{mol}) measurement at the constant field of 5 kOe and at 5 K. When the irradiation started, the M_{mol} values gradually increased and levelled off after *ca.* 10–30 h. The observed increase in the M_{mol} value indicates that the diazo moieties were photolyzed to form the carbene. The plots of M_{mol} vs. irradiation time for the samples of **D2py** and the 1:4 mixture of CoCl₂ and **D2py** are shown in Fig. S2.† The degrees of the photolysis in frozen solution were determined by the consumption of diazo moiety in IR spectra after SQUID measurements. **DYpy** and CoCl₂(**DYpy**)₄ showed quantitative and over *ca.* 95% photolysis, respectively.

(A) **DYpy**; Y = 2, 3l, 3b and 4. 2–10 mM solutions of **DYpy** in MTHF were used for the samples. In order to determine the



Fig. 1 Vis spectra changes of a 1:4 mixture of CoCl₂ and **D2py** in MTHF solution (a) on cooling in the temperature range of 280–175 K before irradiation and (b) on photolysis at 10 K. Inset in (a) shows the spectra in the near IR region. Arrows indicate the increase and decrease of the absorption.

ground state multiplicity after irradiation of **DYpy**, the field dependencies of magnetization before and after irradiation at 2 and 5 K were measured. The $M_{\rm mol}$ vs. H/T plot for **DYpy**; **Y** = **2**, **31**, **3b**, and **4**, in frozen solution, in which $M_{\rm mol} = M_{\rm a} - M_{\rm b}$ ($M_{\rm a}$ and $M_{\rm b}$ are the molar magnetization after and before irradiation, respectively), are shown in Fig. 2 together with theoretical curves with S = 4/2, 6/2, and 8/2, respectively.

All experimental data nearly traced on the theoretical curves^{7,13} for the corresponding *S* values, indicating that carbene centers generated by photolysis interacted ferromagnetically to form the high-spin species in the quintet, septet, septet, and nonet ground state for **CYpy**; **Y** = **2**, **3l**, **3b**, and **4**, respectively.^{14,15} After annealing above 80 K, the magnetization data completely returned to the levels before irradiation.

(B) $CoCl_2(py)_4$ and $CoCl_2(DYpy)_4$; Y = 2, 3l, 3b, and 4. The magnetic properties of $[CoCl_2(py)_4]$ having no organic spin in the crystalline state and those before and after irradiation of 1 : 4 complexes, $CoCl_2(DYpy)_4$; Y = 2, 3l, 3b, and 4, in frozen solutions were investigated by SQUID magneto/susceptometry. The magnetic property for $CoCl_2(D1py)_4$ under frozen conditions was already reported.^{5b}

(*B-1*) $CoCl_2(py)_4$. The values of dc molar magnetic susceptibility, χ_{mol} , for a microcrystalline sample of $[CoCl_2(py)_4]$ were collected at a constant field of 5 kOe. The obtained χ_{mol} values were plotted as a function of temperature. The ac magnetic susceptibilities were measured in the absence and presence of a 3



Fig. 2 M_{mol} vs. H/T plots at 2.0 (open) and 5.0 K (filled) for **D2py** (red circle), **D3lpy** (blue square), **D3bpy** (green triangle), and **D4py** (orange reversed triangle) in MTHF frozen solution after irradiation. Solid lines show the theoretical curves with S = 4/2, 6/2, and 8/2.



Fig. 3 Plots of (a) $\chi_{mol} T vs. T$ at dc field of 5 kOe and (b) $\chi''_{mol} vs. T$ with a 5 Oe ac field oscillating at 1000 (red), 750 (blue), 500 (black), 400 (green), 250 (purple) and 100 (brown) Hz in the presence of a 3 kOe dc field for a microcrystalline sample of $[CoCl_2(py)_4]$. The solid lines for (a) and (b) indicate the fitting curves and the visual guides, respectively.

kOe dc field with a 5.0 Oe ac field at the frequencies of 1000, 750, 500, 400, 250 and 100 Hz in the temperature range of 1.9–6.5 K. The plots of $\chi_{mol}T$ vs. T and χ''_{mol} vs. T in the presence of dc field are shown in Fig. 3.

In the $\chi_{mol}T$ vs. T plot, the $\chi_{mol}T$ values were constant (2.7 cm³ K mol⁻¹) in the temperature range of 300–150 K, gradually decreased below 150 K, reached nearly a constant of 2.0 cm³ K mol⁻¹ in the range 20–5 K, and then decreased below 5 K. The observed thermal profile of the $\chi_{mol}T$ was analyzed by the following Hamiltonian (eqn (1)) in the MAGSAKI program^{16,17} to afford $\Delta = -197$ K, $\kappa = 0.79$, and $\lambda = -887$ K.

$$H = \Delta(\boldsymbol{L}_{z}^{2} - 2/3) - (3/2)\kappa\lambda\boldsymbol{L} \times \boldsymbol{S} + \beta[-(3/2)\kappa\boldsymbol{L} + g_{e}\boldsymbol{S}] \times H$$
(1)

in which Δ is the axial splitting parameter, κ is the orbital reduction factor, and λ is the spin-orbit coupling parameter. The obtained values were comparable to those for a high spin cobalt(II) having an octahedral structure.^{5,8,16,17} The fitting result is shown in Fig. 3a.

In ac magnetic susceptibility measurements, the χ'_{mol} and χ''_{mol} signals (in-phase and out-of-phase components of ac magnetic susceptibilities, respectively) and their frequency dependence were observed, indicating that slow magnetic relaxation existed in [CoCl₂(py)₄]. In the χ''_{mol} vs. T plots, frequencydependent χ''_{mol} signals with no maximum were observed above 1.9 K. To suppress the pathway due to the spin quantum tunneling magnetization (QTM), the dc external field was applied and the ac magnetic susceptibility was measured under similar conditions. The maxima of χ''_{mol} signals with individual frequency were observed in the presence of dc field of 3 kOe (Fig. 3b). The observed peak-top temperature of χ''_{mol} signals depended on the frequency and it shifted to the higher temperature with increasing the frequency. Because each frequency at the peak-top temperature for χ''_{mol} is consistent with τ^{-1} , the effective activation energy, $U_{\rm eff}/k_{\rm B}$, for reversal of the magnetism and the pre-exponential factor, τ_0 , can be obtained in terms of the equation, $\tau =$ $1/(2\pi v) = \tau_0 \exp(U_{\text{eff}}/k_{\text{B}}T)$. From the Arrhenius plot, the $U_{\text{eff}}/k_{\text{B}}$ value of 16 K in the presence of 3 kOe was obtained. These results indicated that a 1:4 cobalt complex essentially had a SMM property showing slow magnetic relaxation, which was strongly affected by the QTM effect, and also suggested the role of organic spin, carbene, in the following heterospin SMM complexes. The $\chi'_{mol}T$ vs. T plot and Arrhenius plot for $[CoCl_2(py)_4]$ are shown in Fig. S3.[†]

(B) $CoCl_2(DYpy)_4$; Y = 2, 31, 3b, and 4. Solutions (5, 2.5, 2.5 and 1.5 mM) of the 1:4 mixtures of CoCl₂ and DYpy; Y = 2, 31, 3b, and 4, respectively, in MTHF were used as samples for SQUID measurements.

Static magnetic properties

(i) $\chi_{mol}T$ vs. T plots. The values of χ_{mol} , before and after irradiation of $CoCl_2(DYpy)_4$; Y = 2, 3l, 3b, and 4, in frozen solution were collected at a constant field of 5 kOe below 20–30 K. The obtained χ_{mol} values were plotted as a function of temperature. The plots of $\chi_{mol}T$ vs. T for $CoCl_2(DYpy)_4$; Y = 2, 3l, 3b, and 4, before and after irradiation are summarized in Fig. 4 together with the plot for $CoCl_2(D1py)_4$.

Before irradiation, the $\chi_{mol}T$ values for four samples were comparable and were nearly constant (2.0 cm³ K mol⁻¹) in the temperature range of 1.9–20 K. The constant value of 2.0 cm³ K mol⁻¹ was consistent with those for [CoCl₂(py)₄] and Co



Fig. 4 $\chi_{mol}T$ vs. T plots below 30 K before (cross) and after irradiation of 1:4 mixtures of CoCl₂ and **DYpy**; **Y** = 1^{5b} (red circle), **2** (blue square), **3l** (green reversed triangle), **3b** (black triangle), and **4** (purple filled circles) in frozen MTHF solutions.



Fig. 5 Hysteresis loops at 1.9 K after irradiation of 1:4 mixtures of CoCl₂ and **DYpy**; **Y** = **1** (red), **2** (blue), **31** (green), **3b** (black), and **4** (purple) in frozen MTHF solution with a sweeping rate of 0.36 kOe s⁻¹.

(Cl)₂(D1py)₄ reported previously.^{5b} After irradiation, the $\chi_{mol}T$ values increased greatly and those at 10 K were 29, 46, 44, and 83 cm³ K mol⁻¹ for CoCl₂(DYpy)₄; Y = 2, 3l, 3b, and 4, respectively. The values at 10 K were much larger than the theoretical values (6, 14, 26, 42 cm³ K mol⁻¹ for Y = 2, 3l, 3b, and 4, respectively) calculated by a spin-only equation with four isolated high-spin carbenes and one high-spin cobalt(II) ion^{5b,8} with effective spin $S'_{eff} = 1/2$ and $g_{eff} = 4.0$, suggesting that the carbenes and the cobalt ions in the complex interacted ferromagnetically to form a high-spin ground state. On cooling, the $\chi_{mol}T$ values were nearly constant in the range 10–20 K and gradually decreased at lower temperatures. The decrease in the $\chi_{mol}T$ values below 5 K indicated an effect of the zero-field splitting caused by spin-orbit coupling in the cobalt ion.⁸ The observed thermal profiles were similar to that for CoCl₂(C1py)₄.

(ii) Hysteresis loops. The field dependencies of molar magnetization, M_{mol} , for all the samples of CoCl₂(CYpy)₄; Y = 2, 31,

3b, and 4, were measured at a field scanning rate of 0.36 kOe s^{-1} in the range of -50 to 50 kOe and in the temperature range of 1.9-3.5 K. When the dc field increased from 0 to 50 kOe, the $M_{\rm mol}$ values gradually increased until 50 kOe. The $M_{\rm mol}$ values at 50 kOe were 6.3 \times $10^4,$ 9.5 \times $10^4,$ 9.7 \times $10^4,$ and 1.2 \times 10^5 cm^3 Oe mol⁻¹ for CoCl₂(CYpy)₄; Y = 2, 31, 3b, and 4, respectively, and they did not reach the saturation magnetization, $M_{\rm s}$, even at 50 kOe, suggesting that the complexes had a large magnetic anisotropy. All of the cobalt complexes, CoCl₂(CYpy)₄, exhibited hysteresis with respect to the applied field. The loops of hysteresis depended on the temperature; they appeared below ca. 3.5 K and the area inside the loop increased upon decreasing the temperature. The observed temperature-dependent hysteresis loop is one of the magnetic behaviors typical to a SMM. The temperature dependencies of hysteresis loops for CoCl₂(CYpy)₄; Y = 2, 3l, 3b, and 4, are shown in Fig. S4⁺ including a H_c , and M_r vs. T plot (inset). The hysteresis loops at 1.9 K for CoCl₂- $(CYpy)_4$; Y = 2, 3l, 3b, and 4, are summarized in Fig. 5 together with $CoCl_2(C1py)_4$. The values of coercive force, H_c , and remnant magnetization, $M_{\rm r}$, at 1.9 K were 12 and 3.0×10^4 , 8.4 and 3.6×10^4 , 11 and 3.9×10^4 , and 8.1 kOe and 5.1×10^4 cm³ Oe mol⁻¹ for CoCl₂(CYpy)₄; Y = 2, 3l, 3b, and 4, respectively, and were larger than those (7.0 kOe and 1.1×10^4 cm³ Oe mol^{-1} , respectively) for CoCl₂(C1py)₄.^{5b}

Dynamic magnetic properties

The magnetization relaxation time in a high and a low temperature region after irradiation of the 1:4 complexes, CoCl₂- $(\mathbf{D}\mathbf{Y}\mathbf{p}\mathbf{y})_4$; $\mathbf{Y} = \mathbf{2}$, **31**, **3b**, and **4** were investigated by ac and dc magnetic susceptibility measurements.

(i) Ac magnetic susceptibility measurements. The ac magnetic susceptibilities of the MTHF solution samples for the 1:4 complexes, $CoCl_2(DYpy)_4$; Y = 2, 3l, 3b, and 4, after irradiation were measured in a zero dc field with a 5.0 Oe ac field in the temperature range of 1.9–10 K. After irradiation, the χ'_{mol} and χ''_{mol} signals with frequency dependence were clearly observed. The intensities of both signals increased in the order of CoCl₂- $(CYpy)_4$; Y = 2, 3l, 3b, and 4 and the relative intensity of χ''_{mol} signals with χ'_{mol} signal were in the region of 0.2–0.3, which is consistent with that reported for SMM previously.9 Observations of χ'_{mol} and χ''_{mol} signals indicated that cobalt complexes have slow magnetic relaxations for reversal of the magnetism. The plots of $\chi'_{mol}T$ vs. T and χ''_{mol} vs. T after irradiation of the 1 : 4 mixtures of $CoCl_2(CYpy)_4$; Y = 2, 31, 3b, and 4, are shown in Fig. S5[†] and Fig. 6, respectively. In the plots of $\chi'_{mol}T$ vs. T, the values of $\chi'_{mol}T$ for CoCl₂(**CYpy**)₄; **Y** = **2**, **3l**, **3b**, and **4**, are 37.5, 55.1, 59.3, and 85.5 cm³ K mol⁻¹ at 10 K, respectively, and remained essentially constant on cooling until the onset of the contribution of χ''_{mol} signals. The constant $\chi'_{mol}T$ values were larger than those obtained in $\chi_{mol}T$ vs. T plots, suggesting that in static measurements and saturation of the magnetic susceptibility might take place in the constant dc field of 5 kOe. From the constant $\chi'_{mol}T$ value of 37.5 cm³ K mol⁻¹, $CoCl_2(C2py)_4$ was estimated to be $S_{total} = 17/2$ and g = 2.0. In $CoCl_2(CYpy)_4$; Y = 3l, 3b, and 4, however, the obtained constant $\chi'_{mol}T$ values deviated from the theoretical ones (84.4 and 144 cm³ K mol⁻¹ for CoCl₂(CYpy)₄; $\mathbf{Y} = \mathbf{3}$ and $\mathbf{4}$, respectively,



Fig. 6 $\chi''_{mol} vs. T$ plots after irradiation of a 1 : 4 mixture (5.0–1.5 mM) of CoCl₂ and **DYpy**; **Y** = (a) **2**, (b) **3l**, (c) **3b**, and (d) **4**, in frozen MTHF solution with a 5 Oe ac field oscillating at 1000 (red), 500 (blue), 100 (black), 10 (green), 5 (deep red) and 1(brown) Hz. The solid lines are visual guides.

assuming g = 2.0). The observed discrepancy might be caused by the intramolecular antiferromagnetic interaction between the polycarbene chains and/or the contribution of the thermal excited state, which is often observed in the complexes with large spin multiplicity.^{2c,18} Below 8 K, $\chi'_{mol}T$ values decreased with frequency-dependence, while the χ''_{mol} signals appeared at the same temperature. In χ''_{mol} vs. T plots for CoCl₂(CYpy)₄; Y = 2, 3l, 3b, and 4, the χ''_{mol} signal intensities increased with increasing Stotal and the peak-top temperatures for each frequency were nearly constant. From χ''_{mol} vs. T plots, the values of $U_{\rm eff}/k_{\rm B}$ and τ_0 were estimated to be 94 and 6.2 \times 10⁻¹¹, 92 and 6.6×10^{-11} , 93 and 4.2×10^{-11} , and 87 K and 1.0×10^{-10} s, for $CoCl_2(CYpy)_4$; Y = 2, 3l, 3b, and 4, respectively. Arrhenius plots for $CoCl_2(CYpy)_4$; Y = 2, 31, 3b, and 4, are shown in Fig. 8 and Fig. S7.^{\dagger} In addition, the blocking temperature, $T_{\rm B}$, defined by the peak-top temperature at 0.01 Hz in the Arrhenius plot was estimated to be 3.3, 3.2, 3.3, and 3.2 K for CoCl₂- $(CYpy)_4$; Y = 2, 3l, 3b, and 4, respectively. These temperatures were consistent with those starting to appear in the hysteresis loops (Fig. S4[†]).

(ii) Dc magnetization decay measurements. To characterize the slow magnetization relaxation at even lower temperatures, dc magnetization decay experiments were carried out at 7-8 temperatures in the range of 1.9–3.3 K for $CoCl_2(CYpy)_4$; Y = 2, 3l, **3b**, and **4**. After the cycle of applying the external field of 50 kOe at 10 K, cooling down to the desired temperature, and then reducing to 0 kOe, the magnetizations were measured as a function of time. The magnetization decay was followed for 2 h. For each measurement, the temperature was raised to 10 K once and then cooled to the desired temperature. The magnetization data, M, were normalized against, M_0 , at t = 0 at each temperature and the M/M_0 values were plotted as a function of time. The M/M_0 vs. time plots for $CoCl_2(CYpy)_4$ within 3×10^3 s (50 min) at the given temperatures are shown in Fig. 7 for Y = 2, and in Fig. S6[†] for Y = **31**, **3b**, and **4**. The decay for $CoCl_2(CYpy)_4$; Y = 2, 31, 3b, and 4, became slower on cooling until 1.9 K without reaching the temperature independent decay due to the QTM. The observed decays at the given temperatures for CoCl₂- $(CYpy)_4$; Y = 2, 3l, 3b, and 4, were slower than those for CoCl₂(C1py)₄.



Fig. 7 Dc magnetization decays after irradiation of 1:4 mixtures (5.0 mM) of CoCl₂ and **D2py** at the given temperatures in frozen solution. Solid lines show the fittings by the stretched exponential equation.

All decay data for $CoCl_2(CYpy)_4$; **Y** = **2**, **3l**, **3b**, and **4** were analyzed by a stretched exponential decay (eqn (2)).^{5b,f,19}

$$\ln(M) = \ln(M_0) - \left(t/\tau\right)^B \tag{2}$$

where M_0 is the initial magnetization, τ is the average relaxation time, and *B* is the width of the distribution; B = 1 is a singleexponential decay. The experimental decay data in the region of $M_0/M_0(1.9) > 0.1$ and $M/M_0 < 0.9$, where $M_0(1.9)$ is M_0 at 1.9 K, at the given temperature were selected and used for the fitting. Under this condition, the measurable value of τ were *ca*. 5×10^2 $< \tau < ca$. 5×10^5 s. The obtained τ values at the given temperatures are listed in Table S1[†] and the fitting curves are shown in Fig. 7 and Fig. S6[†] as solid lines.

(iii) Magnetic relaxations in CoCl₂(CYpy)₄; Y = 2, 3l, 3b, and 4. In SMM, the characteristic slow magnetic relaxation for the reverse of the magnetism takes place in two pathways due to the thermal activation barrier and the spin quantum tunneling magnetization (QTM). The relaxations due to the former are temperature-dependent and obtained by the ac magnetic susceptibility technique, while those due to the latter are temperatureindependent and determined by the temperature dependence of the dc magnetization decay at extremely low temperature. In CoCl₂(CYpy)₄; Y = 2, 3l, 3b, and 4, the dc magnetization decays were combined with those given by means of the ac magnetic susceptibility technique and plotted as a function of inverse *T*. The τ vs. T^{-1} plots are shown in Fig. 8 for CoCl₂(C2py)₄ together with data for CoCl₂(C1py)₄ and in Fig. S7† for the others.

At higher temperatures, the decay times obeyed the Arrhenius law affording the U_{eff}/k_B values. From the ac magnetic susceptibility experiments, the values of U_{eff}/k_B were estimated to be 94, 92, 93, and 87 K for CoCl₂(**CYpy**)₄; **Y** = **2**, **31**, **3b**, and **4**, respectively. In the lower temperature region of 1.9–3.0 K, the relaxation time for CoCl₂(**CYpy**)₄; **Y** = **2**, and **31** collected by the dc magnetization decay slightly deviated downward from the extrapolation of the linear Arrhenius plot obtained by the ac



Fig. 8 τ vs. T^{-1} plots of the data collected by ac magnetic susceptibility technique (open) and dc magnetization decay (filled) after irradiation of a 1 : 4 mixture of CoCl₂ and DYpy; $Y = 1^{5b}$ (triangle) and 2 (circle) in MTHF frozen solution. The solid line is the least-squares fit of the ac data for CoCl₂(C2py)₄, according to the Arrhenius equation.

magnetic susceptibility technique and those for $CoCl_2(CYpy)_4$; Y = 3b, and 4, showed no deviation. The observed deviations suggested that in the low-temperature region (<3.0 K), the relaxation for $CoCl_2(CYpy)_4$; Y = 2, and 31 were weakly affected by the QTM process and those for $CoCl_2(CYpy)_4$; Y = 3b, and 4, were not. Although the values of τ_q for CoCl₂(**CYpy**)₄ could not be directly determined, those must be longer than 10° s. On the other hand, It has been reported that the relaxation time for $CoCl_2(C1py)_4$ collected by the ac magnetic susceptibility technique and the dc magnetization decay were clearly distinguishable and the $U_{\rm eff}/k_{\rm B}$ and $\tau_{\rm q}$ values were determined to be 91 K from the ac magnetic susceptibility experiment and 3.5×10^3 s from the temperature independent dc magnetization decay, respectively.^{5b} These results might suggest that the τ_q value depended on the spin multiplicity of the complex and increased with increasing the S_{total} value. All of the obtained physical magnetic values for the 1:4 complexes, CoCl₂(CYpy)₄ including $CoCl_2(C1py)_4$ in frozen solution are summarized in Table 1.

These results of the dc magnetization decay might suggest that the carbenes strongly affected the transverse interaction, mainly, the rhombic ZFS parameter *E*, relating to QTM and deduced the τ_q rate. In CoCl₂(**CYpy**)₄, the transverse anisotropy of the cobalt ion might become small by the magnetic interaction between the high-spin carbene and the cobalt ion, which increased the τ_q values. The τ_q for CoCl₂(**C1py**)₄ having the smallest *S*_{total} value of 9/2 in CoCl₂(**CYpy**)₄ was already slow enough not to affect the U_{eff}/k_B values. Therefore, the increase of τ_q in CoCl₂-(**CYpy**)₄; **Y** = **2**, **3**], **3b**, and **4**, which had τ_q values over 10² times larger than that for CoCl₂(**C1py**)₄, did not reflect to the U_{eff}/k_B value any more and gave almost the same U_{eff}/k_B values. The increase of τ value from CoCl₂(**C1py**)₄ to CoCl₂(**C2py**)₄ might lead to the increase in H_c of the hysteresis loop.

Conclusion

In SMM, the thermodynamic activation barrier $U/k_{\rm B}$ for the reversal of the magnetism is affected by the spin quantum tunneling magnetization (QTM), leading to the effective activation barrier, $U_{\rm eff}/k_{\rm B}$; $U/k_{\rm B} > U_{\rm eff}/k_{\rm B}$. In [CoCl₂(py)₄] having no organic spin, interestingly, frequency-dependent $\chi''_{\rm mol}$ signals were observed and the thermal profiles of $\chi''_{\rm mol}$ in the presence of a dc field for suppression of the QTM pathway afforded $U_{\rm eff}/k_{\rm B}$ of 16 K, indicating that [CoCl₂(py)₄] was an SMM and was strongly affected by the contribution of QTM. The 1:4 complexes, CoCl₂(**CYpy**)₄; **Y** = **2**, **3**], **3b**, and **4**, with $S_{\rm total} = 17/2$, 25/2, 25/2, and 33/2, respectively, were also SMMs, whose

 $U_{\rm eff}/k_{\rm B}$ values were independent of the $S_{\rm total}$ values and were 94, 92, 93, and 87 K, respectively. On the other hand, the relaxation time of QTM affecting the $U/k_{\rm B}$ depended on the $S_{\rm total}$ values and was suggested to increase with increasing the $S_{\rm total}$ value. The $\tau_{\rm q}$ values of QTM time were estimated to be over 10⁵ s, which did not reflect the $U_{\rm eff}/k_{\rm B}$ value any more.

This study suggests that organic spins, carbenes, attaching at equatorial positions in the octahedral cobalt complexes, $CoCl_2$ -(**CYpy**)₄, ferromagnetically interacted with the cobalt ion through the pyridine ring to increase the relaxation time of QTM. In the 1:4 complexes $CoCl_2(CYpy)_4$, $CoCl_2(C1py)_4$ having the smallest S_{total} value of 9/2 already had a large τ_q value of 10^3 s. To reduce the S_{total} value of the complex and further clarify the role of organic spin in heterospin SMM, investigations of the magnetic properties of the 1:2 complexes of bidentate cobalt complex with **CYpy** are in progress.

Experimental methods

General methods

Infrared spectra were recorded on a JASCO 420 FT-IR spectrometer. UV-Vis and visible-near infrared spectra were recorded on a JASCO V570 spectrometer. ¹H NMR spectra were measured on a JEOL 270 Fourier transform spectrometer using CDCl₃, CD₂Cl₂, and CD₃OD as solvent and referenced to tetramethylsilane. FAB mass spectra (FAB MS) were recorded on a JEOL JMS-SX102 spectrometer. ESI mass spectra (ESI MS) were recorded on a Bruker Daltonics microTOF spectrometer. Melting points were obtained with a MEL-TEMP heating block and are uncorrected. Elemental analyses were performed in the Analytical Center of the Faculty of Science in Kyushu University.

Visible-near infrared spectra measurements at cryogenic temperature

Visible-near infrared spectra were recorded on a JASCO V570 spectrometer attached with an NACC cryo-system LTS-22X for the low temperature measurements. The solution samples were placed in separable quartz cells (path length; 1 mm or 1 cm) under a helium atmosphere. Photolysis of diazo samples were performed by an argon ion laser (514 nm, 200 mW, Omnichrome 543–200 M).

Table 1 Values of S_{total} , $U_{\text{eff}}/k_{\text{B}}$, τ_0 , τ_q , H_c , and M_r , for CoCl₂(**CYpy**)₄; **Y** = **1**, **2**, **31**, **3b**, and **4**, in MTHF frozen solution

Complexes	Stotal	$U_{\rm eff}/k_{\rm B}~({\rm K})$	τ_0 (s)	$\tau_{q}(s)$	$H_{\rm c}$ (kOe)	$M_{\rm r}~({\rm cm}^3~{\rm Oe}~{\rm mol}^{-1})$
$CoCl_2(C1pv)_4^a$	9/2	91	1.2×10^{-10}	3.5×10^{3}	7.0	1.1×10^{4}
$CoCl_2(C2pv)_4$	17/2	94	6.2×10^{-11}	$>5 \times 10^{5}$	12	3.0×10^{4}
$CoCl_2(C3lpv)_4$	25/2	92	6.6×10^{-11}	$>5 \times 10^{5}$	8.4	3.6×10^{4}
$CoCl_2(C3bpv)_4$	25/2	93	4.2×10^{-11}	$>5 \times 10^{5}$	11	3.9×10^{4}
$CoCl_2(C4py)_4$	33/2	87	1.0×10^{-10}	$>5 \times 10^{5}$	8.1	5.1×10^{4}
^a Ref 5h						

" Ref. 5b.

Magnetic measurements

Ac and dc magnetic susceptibility data were obtained on Quantum Design MPMS2 (0 ± 10 kOe) and MPMS-5S (0 ± 50 kOe) SQUID magneto/susceptometries, respectively.

(A) Preparation of solution samples. Solutions (1.5-5 mM) of the samples for the SQUID measurements were obtained as follows: a solution (1 ml) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3–10 mmol) in MTHF and a solution (1 ml) of **DYpy** (12–40 mmol) in MTHF were mixed and used as samples.

(B) General procedure for SQUID measurement in frozen solution. The sample solution was lightly degassed by bubbling nitrogen gas and 50 µl of sample solution was placed into the capsule with a microsyringe (Hamilton Co). The capsule was attached to a handmade SQUID sample rod for the photolysis by a straw. The ac and dc magnetic susceptibility measurements were performed in the temperature range of 1.9–10 and 1.9–20 or 30 K, respectively, before and after irradiation. The irradiation system was reported previously.^{5g} Before irradiation, the $\chi_{mol}T$ values for all samples in the range of 1.9–20 K were nearly constant at *ca*. 1.9–2.1 cm³ K mol⁻¹ for CoCl₂(**DYpy**)₄ respectively. The magnetic susceptibility of MTHF solution itself was measured under similar conditions and was used as the control data.

The samples were taken out of the apparatus after SQUID measurements and were measured by IR spectra on KBr pellets. The quantitative photolysis of the samples were confirmed by the difference of the absorption due to the diazo moiety ($\sim 2050 \text{ cm}^{-1}$) before and after irradiation.

Materials

Unless otherwise stated, the preparative reactions were carried out under a high purity dry nitrogen atmosphere. Diethylether, tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF) were distilled from sodium benzophenone ketyl. Dichloromethane and dimethylsulfoxide were distilled under high-purity N₂ after drying with calcium hydride. [CoCl₂(py)₄] was prepared in a manner similar to the procedure reported previously.¹²

4 To the solution of 3-bromodiphenylmethane 1 (3.0 g, 12.1 mmol) in anhydrous THF (30 ml) was added 1.6 M solution of n-butyllithium (14.7 ml, 24.3 mmol) in n-hexane at -78 °C and was stirring for 2 h. Subsequently, 4-formylpyridine (2.5 g, 24.3 mmol) in anhydrous THF (5 ml) was added dropwise and the reaction mixture was stirred for 4 h at -78 °C. The reaction was quenched with saturated aqueous ammonium chloride. The solution was extracted with CHCl₃ for three times. The organic layers were combined and dried on sodium sulfate. After filtration, organic solvent was evaporated with a rotary evaporator. The obtained residue was chromatographed on silica gel with *n*-hexane : $CHCl_3 = 1 : 1$, and then $CHCl_3 : MeOH = 100 : 1$ as eluents to give carbinol 4 (2.1 g, 7.6 mmol) as pale yellow oil in a 63% yield; IR (NaCl plate) 3421, 1599 cm⁻¹; ¹H NMR $(CDCl_3, 270 \text{ MHz}) \delta 8.50 \text{ (d}, J = 6.0 \text{ Hz}, 2\text{H}), 7.31(\text{s}, 1\text{H}), 7.27$ (d, J = 6.0 Hz, 2H), 7.20–7.14 (m, 8H), 5.75 (s, 1H), 3.97 (s, 2H), 2.80 (br, 1H); Mass spectrum (ESI) m/z Calcd for $(C_{19}H_{17}NONa)^+$ 298.1202. Found: 298.1197.

O2py To a solution of 3.6 g (7.6 mmol) of 4 in acetic acid (25 ml) was added sodium perchromate dihydrate (9.1 g, 30.4 mmol). The reaction mixture was stirred and refluxed for 5 h. The suspension solution was poured into ice water, and KOH (5.0 g), CHCl₃ (20 ml), and MeOH (10 ml) were added into the suspension. After filtration, the solution was extracted with CHCl₃ (50 ml \times 5) and dried with MgSO₄. After filtration, the organic solvent was evaporated with a rotary evaporator and the obtained yellow crude solid was chromatographed on silica gel with CHCl₃ (only) ~ CHCl₃ : MeOH = 100 : 1 as eluents to give O2py as a white solid in a 69% yield (1.6 g, 5.2 mmol). Mp 124–127 °C; IR (KBr disc) 1661, 1597 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 8.84 (d, J = 6.2 Hz, 2H), 8.22 (s, 1H), 8.10-8.04 (m, 2H), 7.82 (d, J = 6.2, 2H); Mass spectrum (ESI) m/z Calcd for $(C_{19}H_{13}NO_2Na)^+$ 310.0838. Found: 310.0828; Anal. Calcd for C₁₉H₁₃NO₂: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.44; H, 4.51; N, 4.67.

5 This was prepared in a manner similar to the procedure for **4** using **2** (1.2 g, 3.6 mmol) in place of **1**. The crude mixture was chromatographed on silica gel with CHCl₃: MeOH = 49 : 1 as eluents to give carbinol **5** (0.7 g, 1.9 mmol) as yellow oil in a 53% yield. IR (NaCl plate) 3359, 1600 cm⁻¹; ¹H NMR (CD₃OD, 270 MHz) δ 8.42 (d, *J* = 6.0 Hz, 2H), 7.40 (d, *J* = 6.0 Hz, 2H), 7.23–7.12 (m, 10H), 7.01 (br, 3H), 5.72 (s, 1H), 3.90 (s, 2H), 3.89 (s, 2H), 1.10 (br, 1H); Mass spectrum (ESI) *m/z* Calcd for (C₂₆H₂₃NONa)⁺ 388.1672. Found 388.1670.

O3lpy This was prepared in a manner similar to the procedure for **O2py** by using **5** (1.0 g, 2.7 mmol) in place of **4**. The crude mixture was chromatographed on silica gel with CHCl₃ : MeOH = 49 : 1 as eluents to give triketone **O3lpy** (0.8 g, 2.2 mmol) as a white solid in a 78% yield. Mp 188–192 °C; IR (KBr disc) 1661, 1598 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 8.84 (d, J = 6.1 Hz, 2H), 8.22 (s, 2H), 8.13–8.04 (m, 4H), 7.83 (d, J = 6.7 Hz, 2H), 7.72–7.59 (m, 3H), 7.62 (d, J = 6.1 Hz, 2H), 7.51 (t, J = 7.4 Hz, 2H); Mass spectrum (ESI) *m*/*z* Calcd for (C₂₆H₁₇NO₃Na)⁺ 414.1101. Found 414.1095; Anal. Calcd for C₂₆H₁₇NO₃: C, 79.78; H, 4.38; N, 3.58. Found: C, 79.26; H, 4.35; N, 3.56.

6 To a solution of 3,3'-dibromodiphenylmethane **3** (6.0 g, 18.5 mmol) in anhydrous THF (60 ml) were added a 1.57 M solution of n-butyllithium (13 ml, 20.4 mmol) in n-hexane at -78 °C and stirred for 2 h. The solution of 3-benzylbenzaldehyde (4.0 g, 20.4 mmol) in anhydrous THF was added dropwise. The reaction mixture was stirred for 1 h at -78 °C and then left to stand overnight at room temperature. The reaction was quenched with saturated aqueous ammonium chloride. The solution was extracted with ether for three times. The organic layers were combined and dried on sodium sulfate. After filtration, organic solvent was evaporated with a rotary evaporator. The obtained residue was chromatographed on silica gel with *n*-hexane : AcOEt = 10:1 as eluents to give carbinol 6 (3.7 g, 8.5 mmol) as a pale yellow oil in a 46% yield. IR (NaCl plate) 3391 cm⁻¹; ¹H NMR (CD₃OD, 270 MHz) δ 7.20–6.96 (m, 17H), 5.59 (s, 1H), 3.81 (s, 4H), 3.90 (br, 1H); Mass spectrum (ESI) m/z 465.08, 467.08 (C₂₇H₂₃BrONa)⁺; Anal. Calcd for C₂₇H₂₃BrO: C, 63.18; H, 4.49. Found: C, 4.35; H, 4.35.

7 To the solution of 6 (3.7 g, 8.4 mmol) in *n*-hexane (50 ml) and CH_3CN (2.7 ml) were added sodium iodide (7.6 g, 50.6 mmol) and chlorotrimethylsilane (6.4 ml, 50.6 mmol). The

solution was stirred for 6 h at room temperature. The reaction mixture was poured into water and extracted by ether (500 ml) three times. The combined ether solutions were washed with sodium thiosulfate and then dried over sodium sulfate. After filtration, ether was removed by reduced pressure. The obtained crude mixture was chromatographed on silica gel with *n*-hexane as an eluent to afford 7 (2.9 g, 6.7 mmol) as a colorless oil in 79.6% yield. IR (NaCl plate) 3025, 2905, 2838 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 7.31–7.10 (m, 11H), 7.01 (d, *J* = 7.5 Hz, 6H), 3.94 (s, 2H), 3.91 (s, 2H), 3.89 (s, 2H); Mass spectrum (ESI) *m*/*z* Calcd for (C₂₇H₂₃BrNa)⁺: 449.0881, 451.0860. Found: 449.0890, 451.0866; Anal. Calcd for C₂₇H₂₃Br: C, 75.88; H, 5.42. Found: C, 76.24; H, 5.41.

8 To anhydrous THF solution (30 ml) stirring at -78 °C was added 1.57 M n-butyllithium (3.5 ml, 5.3 mmol) in n-hexane and then the solution of 7 (1.5 g, 3.5 mmol) in anhydrous THF (15 ml). After stirring for 1.5 h, the solution of 4-formylpyridine (5 ml, 5.3 mmol) in anhydrous THF (15 ml) was added dropwise. The dry ice-acetone bath was removed and the reaction mixture was stirred overnight at room temperature. Saturated ammonium chloride solution was added and the reaction mixture was extracted by ether (200 ml) three times. The combined ether solutions were washed with sodium thiosulfate and then dried over sodium sulfate. After filtration, ether was removed by reduced pressure. The obtained crude mixture was chromatographed on silica gel with $CHCl_3$: MeOH (100:1-10:1) as eluents to afford 8 (0.63 g, 1.4 mmol) as a yellow oil in 39.4% vield. IR (NaCl plate) 3330 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 8.47 (d, J = 6.0 Hz, 2H), 7.28–7.10 (m, 13H), 7.01 (d, J = 8.1Hz, 6H), 5.72 (s, 1H), 3.93 (s, 2H), 3.91 (s, 2H), 3.89 (s, 2H), 2.90 (br, 1H); Mass spectrum (ESI) Calcd for $(C_{33}H_{30}NONa)^+$. 456.2322. Found: 456.2224; Anal. Calcd for C33H29NO: C, 87.00; H, 6.42; N, 3.07. Found: C, 87.87; H, 6.22; N, 2.67.

O4py This was prepared in a manner similar to the procedure for **O2py** using **8** in place of **4**. Reprecipitation from CHCl₃– Et₂O gave tetraketone **O4py** (0.22 g, 2.0 mmol) as a white powder in 32.6% yield. Mp 233–235 °C; IR (KBr disc) 1661, 1598 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 8.84 (d, J = 6.1 Hz, 2H), 8.24 (s, 1H), 8.23(d, J = 7.4 Hz, 2H), 8.12–8.03 (m, 6H), 7.83 (d, J = 7.4 Hz, 2H), 7.71 (d, J = 2.0 Hz, 1H), 7.67 (d, J =6.1 Hz, 2H), 7.63–7.59 (m, 3H), 7.50(t, J = 7.4 Hz, 2); Mass spectrum (ESI) m/z 518.14 (C₃₃H₂₁NO₄Na)⁺; Anal. Calcd for C₃₃H₂₁NO₄: C, 79.99; H, 4.27; N, 2.83. Found: C, 79.28; H, 4.54; N, 2.76.

9 To a solution of 1,3,5-tribromobenzene (3.0 g, 9.5 mmol) in anhydrous THF (120 ml) was added a 1.6 M solution of *n*-butyl-lithium (17.8 ml, 28.5 mmol) in *n*-hexane at -78 °C. After stirring for 4 h, 1-formyl-4-*tert*-butylbenzene (3.0 g, 28.5 mmol) in anhydrous THF (30 ml) was added dropwise. The reaction mixture was stirred for 1 h at -78 °C. Saturated ammonium chloride solution was added and the reaction mixture was extracted by ether (200 ml) three times. The combined ether solutions were dried over sodium sulfate. After filtration, ether was removed by reduced pressure. Crude carbinol (15.2 g, *ca.* 98% yield) containing monoketone derivative was obtained as a brown solid. Sodium borohydride (4.8 g) was added to a solution of crude carbinol in methanol (40 ml). The suspension was stirred and refluxed for 4 h. The solvent was evaporated and the crude mixture was chromatographed on silica gel with CHCl₃:

MeOH = 49 : 1 to give carbinol **9** (11.5 g, 24.2 mmol) as a white solid in a 76% yield. Mp 167–171 °C; IR (KBr disc) 3310 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 7.43 (d, J = 5.4 Hz, 2H), 7.36 (d, J = 8.7 Hz, 4H), 7.34 (s, 1H), 7.25 (d, J = 8.0 Hz, 4H), 5.75 (s, 2H) 1.30 (s 18H); Mass spectrum (ESI) m/z Calcd for (C₂₈H₃₃O₂BrNa)⁺ 503.1556. Found: 503.1554; Anal. Calcd for C₂₈H₃₃O₂Br: C, 69.85; H, 6.91. Found: C, 70.21; H, 6.98.

10 This was prepared in a manner similar to the procedure for 7 using 9 in place of 6. Reprecipitation from CHCl₃–Et₂O gave **10** as a white powder in 85% yield. Mp 68–70 °C; IR (KBr disc) 3024, 2978 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 7.31 (d, J = 8.0 Hz, 4H), 7.16 (s, 2H), 7.08 (d, J = 8.0 Hz, 4H), 7.00 (s, 1H), 3.87 (s, 4H), 1.30 (s, 18H); Mass spectrum (ESI) *m/z* 471.16 (C₂₈H₃₃BrNa)⁺; Anal. Calcd for C₂₈H₃₃Br: C, 74.82; H, 7.40. Found: C, 74.84; H, 7.43.

11 This was prepared in a manner similar to the procedure for 5 using 10 in place of 2. The crude mixture including 11 and 12 was obtained as a yellow oil and used for the next oxidation procedure. Mass spectrum (ESI) m/z Calcd for $(C_{34}H_{39}NO)^+$: 477.3032. Found: 478.3104.

12 Activated MnO₂ (10.4 g, 119.2 mmol) was added to the crude mixture of 11 and 12 (7.6 g) in CHCl₃ (65 ml) and the mixture was refluxed for 6 h. After filtration, the solvent was removed on a rotary evaporator. The crude mixture was chromatographed on silica gel with CHCl₃ (only) ~ CHCl₃ : MeOH = 100 : 1 as eluents to afford 12 (4.0 g, 8.4 mmol) as a white solid in 76% yield in two steps. IR (KBr disc) 1663 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 8.74 (d, *J* = 6.0 Hz, 2H), 7.49 (d, *J* = 6.0 Hz, 2H), 7.46 (s, 3H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.09 (d, *J* = 8.4 Hz, 4H), 3.87 (s, 4H), 1.30 (s, 18H); Mass spectrum (ESI) Calcd for (C₃₃H₃₀NONa)⁺: 456.2322. Found: 456.2224.

O3bpy Sodium perchromate (9.1 g, 30.4 mmol) was added to a solution of 12 (3.6 g, 7.6 mmol) in acetic acid (45 ml). The suspension was stirred and refluxed for 10 h. The reaction mixture was poured into ice water. After filtration, the residue of pale yellow solid was washed with water (50 ml). The filtrate was centrifuged at 3500 rpm for 10 min and the sticky precipitate on the bottom of the test tube was collected. The sticky precipitate was dissolved in MeOH (30 ml), KOH was added until the color of the solution changed to pale green, and the solution was stirred at room temperature overnight. Water (100 ml) was added and the solution was extracted with Et₂O (50 ml) three times, ether layers were combined and dried with MgSO₄. After filtration, ether was evaporated by a rotary evaporator to afford O3bpy (2.6 g, 5.2 mmol) as a white solid in a 69% yield. Mp 230–234 °C; IR (KBr disc) 1663 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 8.86 (d, J = 4.0 Hz, 2H), 8.41 (s, 3H), 7.79 (d, J = 8.0 Hz, 4H), 7.64 (d, J = 4.7 Hz, 2H), 7.54 (d, J = 8.0 Hz, 4H) 1.37 (s, 18H); Mass spectrum (ESI) m/z 526.25 $(C_{34}H_{33}NO_3Na)^+;$ Anal. Calcd for C34H33NO3. 0.1CHCl₃·0.1CH₃CN: C, 79.27; H, 6.48; N, 2.96. Found: C, 79.26; H, 6.76; N, 2.96.

D2py This was prepared by using **O2py** in a manner similar to the procedure reported previously.^{6f} Crude **D2py** was chromatographed on Al₂O₃ with CH₂Cl₂ as eluent and then recrystallized from Et₂O-CH₂Cl₂ to afford **D2py** as red thin plate crystals. Mp (dec.) 108–110 °C; IR (KBr disc), $v_{C=N2}$

2038 cm⁻¹; UV-Vis in CH₂Cl₂, $\lambda_{max}(\varepsilon)$: 294 (3.5 × 10⁴) and 508 (2.1 × 10²) nm; ¹H-NMR (270 MHz, CDCl₃), δ 8.43 (dd, J = 4.6 and 1.7 Hz, 2H), 7.51–7.10 (*m*, 9 H), 7.06 (dd, J = 4.6 and 1.7 Hz, 2H); Mass spectrum (ESI) *m/z* Calcd for (C₁₉H₁₃N₅Na)⁺ 334.1063. Found 334.1048; Anal. Calcd for C₁₉H₁₃N₅: C, 73.30; H, 4.21; N, 22.49. Found: C, 73.16; H, 4.19; N, 22.44.

D3lpy This was prepared by using **O3lpy** in a manner similar to the procedure reported previously.^{6/} Crude **D3lpy** was chromatographed on Al₂O₃ with CH₂Cl₂ as eluent and then re-precipitated from CH₂Cl₂–Et₂O to afford **D3lpy** as red thin plate crystals. Mp (dec.) 74–75 °C; IR (KBr disc), $v_{C=N2}$ 2039 cm⁻¹; UV-Vis in CH₂Cl₂, $\lambda_{max}(\varepsilon)$: 302 (4.6 × 10⁴) and 512 (3.1 × 10²) nm; ¹H-NMR (270 MHz, CD₂Cl₂), δ 8.48 (d, J = 4.9 Hz, 2), 7.50–7.10 (m, 13 H), 7.07 (dd, J = 4.6 and 1.7 Hz, 2H); FAB mass (in NBA matrix), (M + 1)⁺ 428; Anal. Calcd for C₂₆H₁₇N₇: C, 73.05; H, 4.01; N, 22.94. Found: C, 73.09; H, 4.01; N, 22.78.

D3bpy This was prepared by using **O3bpy** in a manner similar to the procedure reported previously.^{6/} Crude **D3bpy** was chromatographed on Al₂O₃ with CH₂Cl₂ as eluent and then recrystallized from ether to afford **D3bpy** as red crystals. Mp (dec.) 95–105 °C; IR (KBr disc) $v_{C=N2}$ 2039 cm⁻¹; UV-Vis in CH₂Cl₂ $\lambda_{max}(\varepsilon) = 294$ (6.2 × 10⁴) and 510 (3.6 × 10²) nm; ¹H NMR (CD₂Cl₂, 270 MHz) δ 8.44 (dd, J = 6.4, 1.7 Hz, 2H), 7.44 (d, J = 8.7 Hz, 4H), 7.25 (d, J = 8.7 Hz, 4H), 7.07 (dd, J = 6.4, 1.7 Hz, 2H), 1.32 (s, 18H); Mass spectrum (ESI) m/z Calcd for (C₃₄H₃₄N₇)⁺ 540.2876. Found 540.2884; Anal. Calcd for C₃₄H₃₃N₇: C, 75.67; H, 6.16; N, 18.17. Found: C, 75.60; H, 6.21; N, 17.95.

D4py This was prepared by using **O4py** in a manner similar to the procedure reported previously.^{6f} Crude **D4py** was chromatographed on Al₂O₃ with CH₂Cl₂ as eluent and then reprecipitated from Et₂O:*n*-hexane (10:1) to afford **D4py** as a red powder in 56.3% yield. Mp (dec.) 96–100 °C; IR (KBr disc) 2039, 1587 cm⁻¹; UV-Vis in CH₂Cl₂ $\lambda_{max}(\varepsilon) = 300 (9.2 \times 10^4)$, 510 ($\varepsilon = 4.2 \times 10^2$) nm; ¹H-NMR (270 MHz, CD₂Cl₂), δ 8.48 (d, J = 4.9 Hz, 2H), 7.50–7.10 (m, 17 H), 7.07 (dd, J = 4.6 and 1.7 Hz, 2H); Mass spectrum (ESI) *m/z* Calcd for (C₃₃H₂₁N₉Na)⁺ 566.1812. Found 566.1788; Anal. Calcd for C₃₃H₂₁N₉: C, 72.92; H, 3.89; N, 23.19. Found: C, 72.85; H, 3.90; N, 23.02.

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