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ON-OFF Luminescence Signaling of Hybrid Organic–Inorganic Switches

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Ⓢ *Supporting Information*

ABSTRACT: The dyads $\mathbf{1}_{\mathbf{OFF}}$ and $\mathbf{2}_{\mathbf{OFF}}$ were prepared by combining the inorganic luminophores $[Ru(phen)_2(2\text{-}[imidazol\text{-}2\text{-}yl]pyridine)]^{2+}$ and $[Re(CO)_3Cl(2\text{-}[imidazol\text{-}2\text{-}yl]pyridine)]$ with 2-(anthracen-9-yl)-4-methylphenol as a second photoactive moiety. In both cases, the inorganic unit operates as the emitter, whereas the organic part acts as a controller. Emission of the inorganic luminophore can be reversibly switched **ON** and **OFF** by adjusting the energetic level of the $^3\pi-\pi^*$ state of the appended anthracene unit through either dearomatization using a photohydration or aromatization applying a thermal dehydration. Emission of both switches is reversibly recorded and erased multiple times without significant degradation.

■ INTRODUCTION

Molecules that reversibly shift their functional behavior in response to one or several external stimuli, such as light, heat, change in pH, electrical field, microenvironment, and so forth, are called molecular switches.[1] While great success stories have been realized with colorimetric devices,[2] luminescent organic switches often show problems with long-term stability of the ON (write) and OFF (erase) states because of aggregation, oxygen quenching, and decomposition.[3] Therefore, researchers have intensified the development of hybrid organic–inorganic switches with the inorganic units acting as the emitter due to the more pronounced stability of their redox states, specifically in presence of heat, light, and water.[4,5] Complementarily, the organic unit takes the part of modulating the inorganic luminophore. For the latter purpose, anthracene derivatives have been frequently used, because they are well-known to quench the ^{3}MLCT emission of numerous second and third row transition metal complexes, such as Ru^{2+}-, Re^{+}-, Pt^{2+} polypyridyls, through $^3\text{MLCT}\rightarrow\ ^3\pi-\pi^*$ energy transfer.[1a,4f,5] The complexes $[Ru(bpy)_2L]^{2+}$ and $[Re(CO)_3(Cl)L]$ with L = *N*-(9-anthracenylmethyl)-2-(2-pyridyl)benzimidazole may serve as representative examples.[6] Neither a ^{3}MLCT based emission (λ_{ex} = 450–470 nm) nor a $^1\pi-\pi^*/^3\pi-\pi^*$ anthracene emission (λ_{ex} = 355–375 nm) were observed at ambient conditions.[6] Based on this design principle, several groups have selectively oxidized the appended anthracene chromophore in Ru/Re-anthracene dyads thus restoring luminescence of the inorganic unit (vide infra).[5,7] Castellano and co-workers[8] have adopted a slightly modified approach using $[Ru(bpy)_2L]^{2+}$ (L = 1-(anthracen-9-yl)-2-(bipyridyl)ethane) as OFF state (Φ < 0.004 in deaerated CH_3CN). The ON state with a considerable MLCT based emission of the ruthenium core ($\Phi \sim 0.06$ in deaerated CH_3CN) was realized by eradicating the lower lying nonradiative $^3\pi-\pi^*$ states of the appended anthracene via photodimerization. The OFF state was regenerated by thermally splitting the photodimer. The same group equally introduced the doubly anthracene-functionalized switch $[Ru(bpy)_2L]^{2+}$ (L = 1-*bis*(anthracenylmethyl)-2-(bipyridyl)ethane)[9] capitalizing on an intramolecular anthracene photodimerization and thermal cycloreversion for luminescence readout and erase cycles. For all of these switches, the authors observed invariable readout stability for multiple cycles without loss in emission intensities. However, emission erase was not complete due to the high stability of the photodimer. All these findings thus indicate that fully reversible luminescent switches can only be achieved through a proper design of the concomitant controller unit.[1a]

Photoexcitation of 2-(anthracen-9-yl)phenol and its derivatives in aqueous solutions is well-known to yield the corresponding hydrated anthracenyl derivatives (triaryl carbinols) through excited state intramolecular proton transfer (ESIPT).[10] Because this process allows manipulation of the energy levels of anthracene,[10e] we utilized our expertise in the field of Ru^{2+}-luminophores[11] to design two novel luminescent switches (Chart 1) with either $[Ru(phen)_2(2\text{-}[imidazol\text{-}2\text{-}yl]pyridine)]^{2+}$ or $[Re(CO)_3Cl(2\text{-}[imidazol\text{-}2\text{-}yl]pyridine)]$ subunits as emitter and the 2-(anthracen-9-yl)-4-methylphenol as a controller. The objective was to modulate luminescence of the inorganic emitter reversibly by manipulating the triplet energy level of the appended 2-(anthracen-9-yl)-4-methylphenol via ESIPT photohydration and subsequent dehydration.

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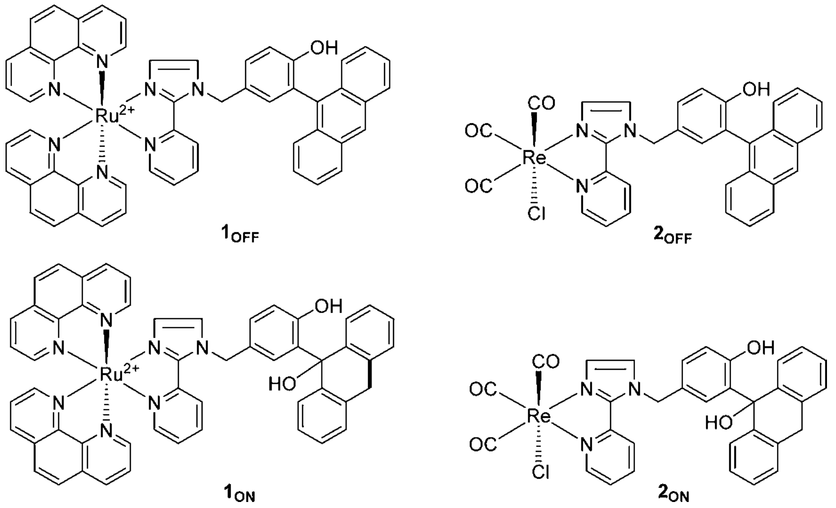
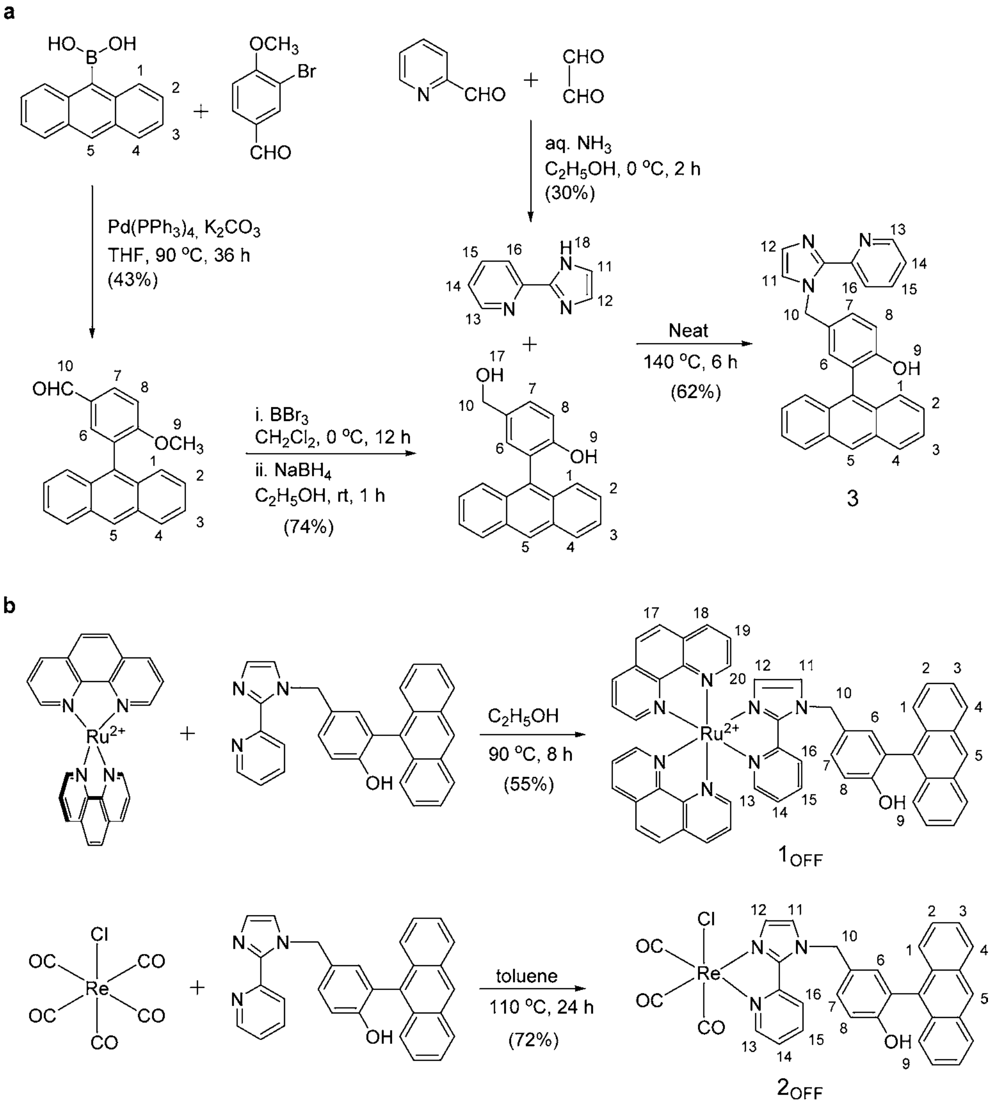
Chart 1. Molecular Structure of Dyads 1_{OFF} and 2_{OFF}, and Their Photo Product 1_{ON} and 2_{ON}, Respectively



Scheme 1. Synthetic Routes to Ligand 3 (a) and Dyads 1_{OFF} and 2_{OFF} (b)[a]



[a] Numbering is only used for ^{1}H NMR assignments and does not reflect IUPAC nomenclature.

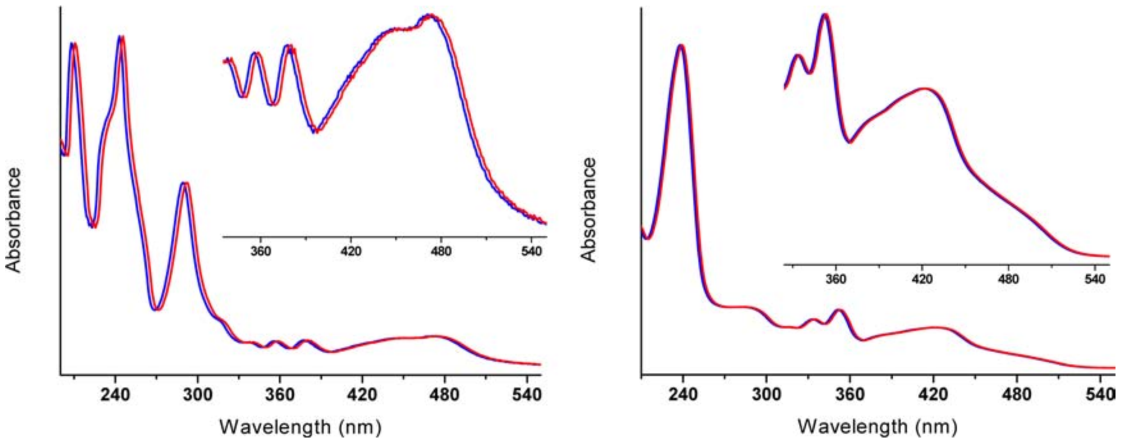


Figure 1. UV−vis absorption spectra of $\mathbf{1}_{\mathrm{OFF}}$ (left) and $\mathbf{2}_{\mathrm{OFF}}$ (right) in air-equilibrated acetonitrile (purple) and 50% aqueous acetonitrile (blue) (1×10^{-4} M) at room temperature.

Table 1. Optical Absorption and PL of $\mathbf{1}_{\mathrm{OFF}}$, $\mathbf{2}_{\mathrm{OFF}}$, $\mathbf{1}_{\mathrm{ON}}$, and $\mathbf{2}_{\mathrm{ON}}$, and Their Model Compounds[a]

compound	λ_{abs} /nm (10^{-4} ε/M^{-1} cm^{-1})[b]	$\lambda_{\mathrm{max}}^{\mathrm{PL}}$ /nm[c]	Φ_{PL}[d]	T$_1$ /(cm^{-1})[e,f]
$\mathbf{1}_{\mathrm{OFF}}$	210 (102), 240 (sh), 255 (106), 293 (62), 340 (sh), 350 (9), 372 (11), 390 (13), 442 (13), 471 (14)	580−670 (b)	$<10^{-3}$	ND
$\mathbf{2}_{\mathrm{OFF}}$	253 (133), 287 (sh), 327 (22), 342 (27), 417 (18)	600−700 (b)	$<10^{-4}$	ND
$\mathbf{1}_{\mathrm{ON}}$	235 (154), 274 (sh), 462 (21)	626	0.0142	17600
$\mathbf{2}_{\mathrm{ON}}$	244 (173), 305(sh), 411 (26)	616	0.0031	18100
$[\mathrm{Ru(phen)_3}]^{2+}$	287, 466	624	0.023[f]	15700[f]
$[\mathrm{Re(Phe\text{-}ImPy)}]^{+}$	239, 414[g]	617[g]	0.0011[h]	16400[g]
9-PA	225, 257, 353, 369, 396	430	0.53[i]	14500[i]

[a]Triplet energy values for model compound are taken from the literature.[19−21]. [b]Absorption spectra were measured in air-equilibrated solutions at 1×10^{-4} M in 50% aqueous acetonitrile. [c]Emission spectra were recorded in air-equilibrated solutions at 1×10^{-5} M in 50% aqueous acetonitrile. [d]PL quantum yields (Φ_{PL}) were determined using $[\mathrm{Ru(bpy)_3}]^{2+}$ as a standard ($\Phi = 0.028$, $\lambda_{\mathrm{exc}} = 450$ nm) in aerated CH_3CN-water solution. [e]The triplet energy of $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$ were estimated from the onset of their emission spectra. [f]Ref 19. [g]Ref 20. [h]Ref 6. [i]Ref 21. Abbreviations: 9-PA, 9-phenylanthracene; T$_1$, triplet energy; sh, shoulder; b, broad; ND, not determined.

Because hydration and dehydration normally occur readily and quantitatively,[12] we expected good signals for readout and full erase capability, thus overcoming the disadvantages of existing switches.[1] Herein, we report the synthesis and the optical, photochemical as well as functional behavior of two hybrid dyads (Chart 1) in aqueous solutions.

■ RESULTS

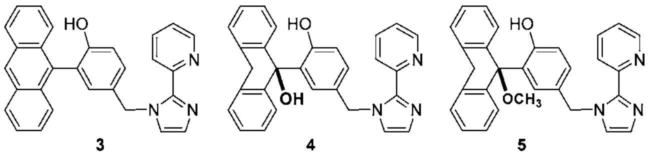
Synthesis. The synthetic approach to ligand **3** and dyads $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ is outlined in Scheme 1.

A typical procedure to prepare alkylimidazoles involves the nucleophilic substitution of alkyl halides by sodium or potassium imidazolates.[13] However, all our attempts to prepare 9-(5-(bromomethyl)-2-methoxyphenyl)anthracene from 9-(2-methoxy-5-methylphenyl)anthracene were met with failure. Hence, ligand **3** was synthesized by a condensation of 2-(imidazol-2-yl)pyridine and 2-(anthracen-9-yl)-4-(hydroxymethyl)phenol at elevated temperature (Scheme 1).[14] The imidazole itself was afforded from the cyclocondensation of pyridine-2-carboxaldehyde, glyoxal, and aqueous NH_3 in ethanol.[15] The anthracene derivative was prepared in a three-step procedure involving a Pd(0) catalyzed Suzuki coupling of 9-anthraceneboronic acid and 3-bromo-4-methoxybenzaldehyde followed by demethylation and reduction (Scheme 1).[16] Compound $\mathbf{1}_{\mathrm{OFF}}$ was prepared by reaction of ligand **3** with $[\mathrm{Ru(phen)_2Cl_2}]$ in ethanol,[11] whereas $\mathbf{2}_{\mathrm{OFF}}$ was synthesized in toluene from $[\mathrm{Re(CO)_5Cl}]$ and ligand **3**.[6] Full characterization of all compounds is provided in the Experimental Section and detailed further in the Supporting Information.

Optical Properties. UV−vis absorption and photoluminescence (PL) spectra of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ were recorded in CH_3CN or in a mixture of CH_3CN-water (50:50) at ambient conditions. In both solvent systems, the absorption spectra of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ were basically the sum of the corresponding subunits' absorptions with only minor differences in wavelength maxima and band shapes (Figure 1 and Table 1). For $\mathbf{1}_{\mathrm{OFF}}$, the spectrum shows two MLCT bands; the lowest energy band at 471 nm corresponds to Ru $(d\pi)\rightarrow\pi^*$ transitions of ligand **3**, whereas the band at 442 nm arises from Ru $(d\pi)\rightarrow\pi^*$ of phenanthrolines.[17] The structured absorptions in the visible region between 350 and 400 nm are the characteristic collection of π−π^* bands of arylanthracene as well as high energy MLCT transitions.[6,18] Besides, the intense absorptions in the UV region between 210 and 280 nm arise by admixture of intramolecular $\pi\rightarrow\pi^*$ transitions from phenanthrolines, 2-(imidazol-2-yl)pyridine and arylanthracene (β-band) moieties.[17,18] Analogous transitions, MLCT as well as intraligand $\pi\rightarrow\pi^*$, were equally noticed in $\mathbf{2}_{\mathrm{OFF}}$ (Figure 1), with the MLCT band being blue-shifted about 54 nm (~ 2750 cm^{-1}) as compared to that of $\mathbf{1}_{\mathrm{OFF}}$.[17] A detailed analysis of the UV−vis profiles indicates that the ground states of both chromophores in $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ are not interfering much, because they are separated by an aliphatic chain. The well-defined separation of their absorption bands allowed selective excitation of both chromophores as of interest. When the PL response of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ (Supporting Information, Figure S1) was evaluated by exciting at 350 to 480 nm using an increment of 10 nm, substantial emission was observed neither from $\mathbf{1}_{\mathrm{OFF}}$ (Φ_{PL} $<10^{-3}$, $\lambda_{\mathrm{ex}} = 450$ nm) nor from $\mathbf{2}_{\mathrm{OFF}}$ (Φ_{PL} $<10^{-4}$, $\lambda_{\mathrm{ex}} = 420$ nm), vide infra.[6,7c,17] The corresponding excitation spectra for $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ were recorded by monitoring MLCT as well as anthracene, based emissions at 630 and 400 nm, respectively, and show quite clearly distinct absorption features suggesting that both chromophores are mutually independent (Supporting Information, Figures S2 and S3).

Photolysis of 3. As outlined above in our project design the well-established ESIPT photohydration of 2-(anthracen-9-yl)-4-methylphenol is considered to switch ON the emission of the inorganic luminophore in $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$. At the onset, we thus examined the photoreactivity of ligand **3** in aqueous solutions to probe the influence of the 2-(imidazol-2-yl)pyridine unit on the photoreactivity of 2-(anthracen-9-yl)-4-methylphenol. Irradiation of **3** at 355 ± 5 nm either in 50% aqueous CH_3CN or in 50% aqueous methanol yielded within 4–5 h the expected 9-hydroxy- or 9-methoxy-10-hydroanthracene derivatives **4** and **5** (Chart 2).[10] Both products were confirmed by NMR, mass spectroscopy, IR and elemental analysis. ^{1}H NMR spectra of ligand **3** and its photoproducts **4** and **5** are shown in Figure 2. Two major changes are visible by comparing the photoproducts with **3** as the reactant. A new peak appears at 3.90–3.96 ppm, while the signal at 8.68 ppm has disappeared. In the ^{13}C NMR, two carbons of the photoproducts dramatically shift upfield to 36.2 and 81.1 ppm from 105.5 and 117.1 ppm in ligand **3**. It is worth noting that ^{1}H NMR spectra of 9-hydroxy-10-hydroanthracenes show a C$\underline{H}_2$ signal at 3.85–3.98 ppm[22] like ligand **3** after photohydration (Figure 2). Thus, the above changes are characteristic for hydration of 2-(anthracen-9-yl)alkylphenols.[22] Reciprocally, ^{1}H and ^{13}C NMR signals of the 2-(imidazol-2-yl)pyridine subunit in ligand **3** were not affected significantly by photolysis indicating that the subunit did not react under the experimental conditions.

Chart 2. Molecular Structure of Ligand 3 and Its Photoproducts 4 and 5



Anthracenes are recognized for their characteristic optical properties.[23] Thus, absorption and PL analysis were used to monitor the photoreactivity of **3** at 30 min intervals. In both channels, the initial absorption/emission intensity of the 2-(anthracen-9-yl)-4-methylphenol residue in **3** decreased gradually with irradiation time as a result of the loss of conjugation.[10] After 4–5 h of constant excitation at $\lambda = 355$ ± 5 nm, the solution of ligand **3** was completely transparent at anthracene absorption and emission wavelengths (Figure 3) suggesting that the photoreactive 2-(anthracen-9-yl)-4-methylphenol chromophore did not exist anymore. Eventually, the following rationalizations were made based on the results of NMR, mass, UV–vis, and PL studies: (i) upon photolysis, the 2-(anthracen-9-yl)-4-methylphenol unit in **3** undergoes the well-known ESIPT process and is quantitatively transformed into the less conjugated hydrated derivative **4**,[10e] (ii) photophysical properties and energy levels of the hydrated anthracenyl residue are quite different from those of the 2-(anthracen-9-yl)-4-methylphenol unit, and (iii) photoreactivity

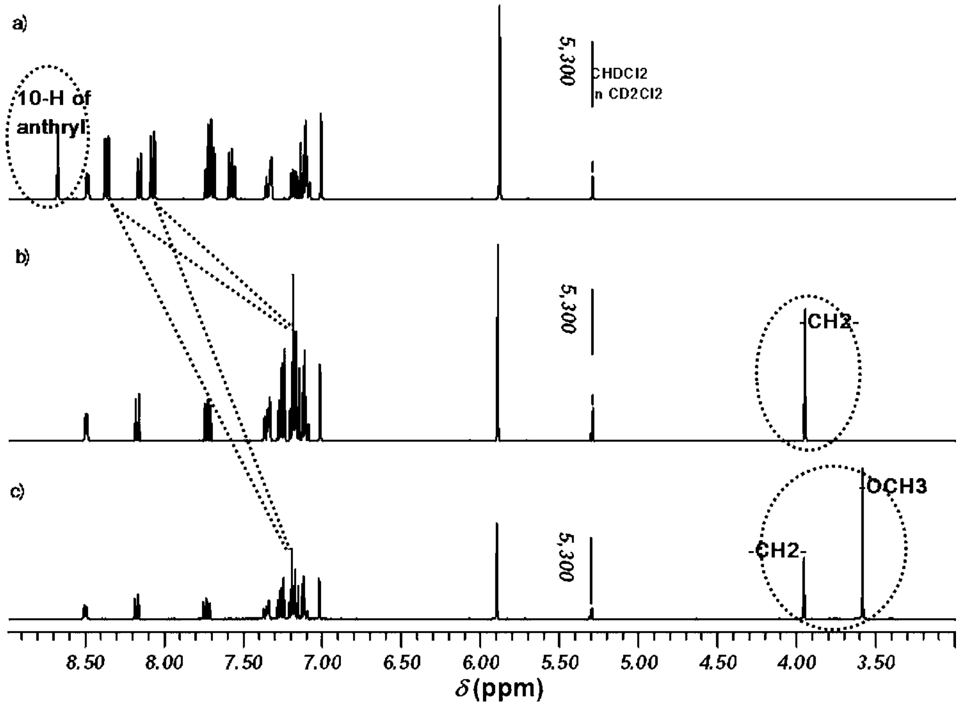


Figure 2. ^{1}H NMR spectra (CD_2Cl_2) of (a) ligand **3** and (b,c) its photoproducts. (b) The photoproduct **4** and (c) the photoproduct **5** are formed after photolysis of **3** in water-acetonitrile and water–methanol, respectively. Notice the diagnostic signals (CH_2, OCH_3) of both products located in the upfield region (marked with a circle). Proton 10-H of the anthracene unit is not present in the aromatic region of the photoproducts.

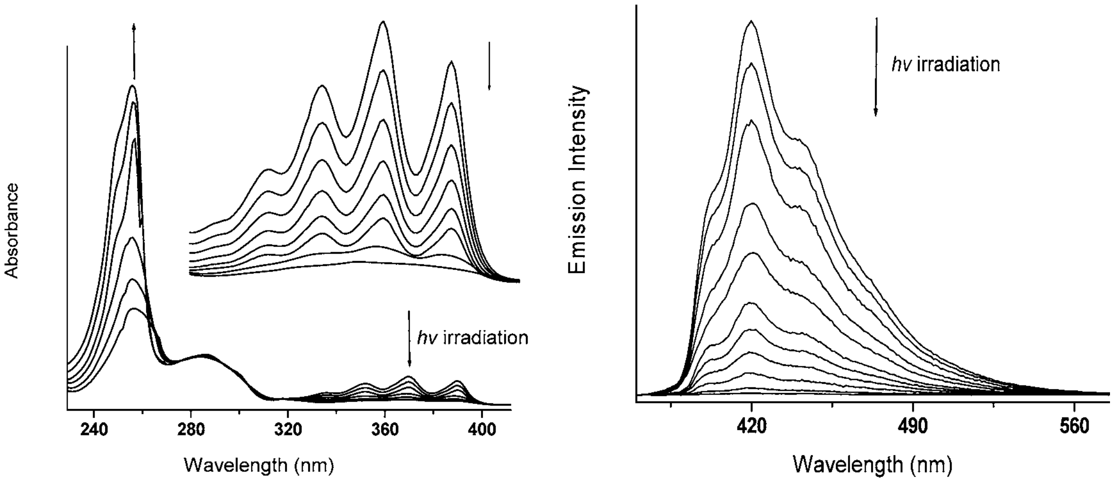


Figure 3. Photochemical reaction of ligand **3** in 50% aqueous CH_3CN (λ_{ex} = 355 ± 5) was monitored at 30 min intervals by UV−vis (left) and luminescence (right) analysis. Notice that the absorption at 240−270 nm increases due to the formation of small aromatic rings from the original anthracenyl subunit, whose absorption and emission intensities decline.

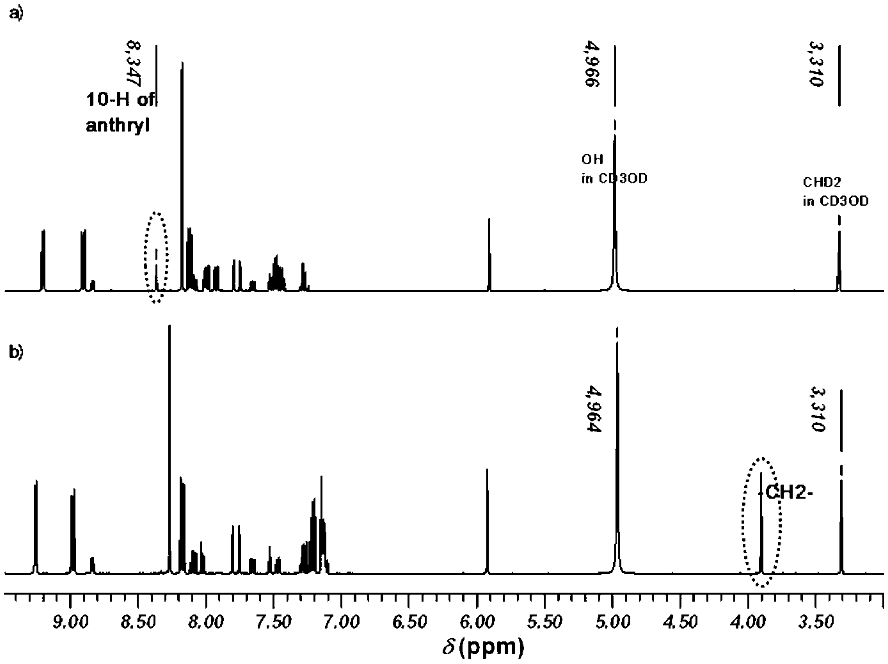


Figure 4. ^1H NMR spectra of (a) $\mathbf{1}_{OFF}$ and (b) its photoproduct $\mathbf{1}_{ON}$ in CD_3OD. Notice the diagnostic signal for CH_2 in $\mathbf{1}_{ON}$ located in the upfield region (marked with a circle). Likewise, anthracene proton 10-H disappeared and other protons (1-H to 8-H) underwent upfield shift in the aromatic region of $\mathbf{1}_{ON}$.

of the 2-(anthracen-9-yl)-4-methylphenol in ligand **3** is not affected substantially by the 2-(imidazol-2-yl)pyridine substituent.

The quantum yield[10a] for photogeneration of **4** (Φ_{pdt} = 0.071 in 50% aqueous CH_3CN) and **5** (Φ_{pdt} = 0.126 in 50% aqueous methanol) (see Chart 2) was assessed through UV−vis absorption measurements (cf. experimental part).

Photolysis of $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$. Both $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ were excited separately in a CH_3CN-water mixture (50:50) under exactly the same conditions as mentioned for **3**. Within 18 h,[24] $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ entirely transformed into the hydrated products $\mathbf{1}_{ON}$ and $\mathbf{2}_{ON}$ (Chart 1),[25] which were isolated and characterized by NMR, mass spectroscopy, and elemental analysis. The ^1H NMR spectra of $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ as well as their photoproducts are shown in Figures 4 and 5. Both photoproducts display a new signal in the aliphatic region, while concurrently an aromatic signal is gone. In addition, after photoexcitation the ^1H NMR peaks of the 2-(anthracen-9-yl)-4-methylphenol units appear upfield shifted by 0.2−0.3 ppm, whereas signals corresponding to the metal complex unit are not affected signifycantly. In all, the detected spectral changes are approximately similar to those noticed for ligand **3** and its photohydrated product **4** (Figure 2).

The time evolution of the photodearomatization of $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ was monitored by absorption and emission measurements. As shown in Figure 6, the absorption bands between 350 and 400 nm arising from the 2-(anthracen-9-yl)-4-methylphenol residue in $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ completely vanished after 18 h of photolysis. In this course, a new peak appeared in the high energy region (λ = 240−255 nm) being diagnostic for the

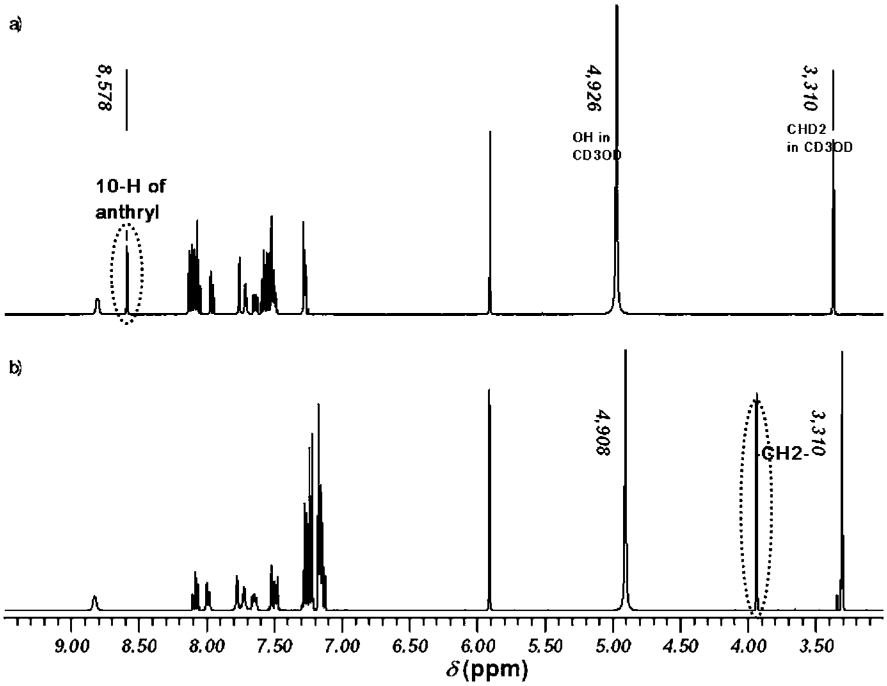


Figure 5. ^{1}H NMR spectra of (a) $\mathbf{2}_{\mathrm{OFF}}$ and (b) its photoproduct $\mathbf{2}_{\mathrm{ON}}$ in CD_3OD. Notice the diagnostic signal for CH_2 in $\mathbf{2}_{\mathrm{ON}}$ located in the upfield region (marked with a circle). Likewise, anthracene proton 10-H disappeared and other protons (1-H to 8-H) underwent upfield shift in the aromatic region of $\mathbf{2}_{\mathrm{ON}}$.

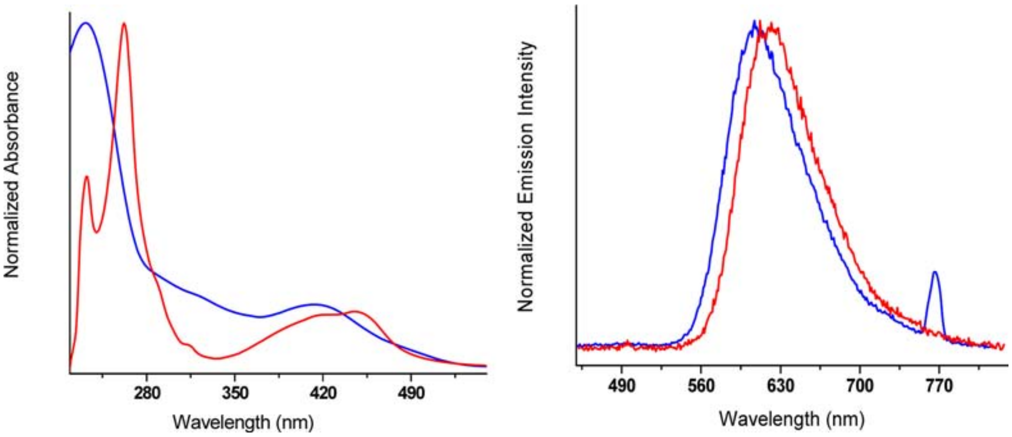


Figure 6. UV–vis (left) and PL (right) spectra measured after 18 h of photoexcitation (λ = 355 ± 5 nm) of $\mathbf{1}_{\mathrm{OFF}}$ (red, λ_{ex} = 450 nm) and $\mathbf{2}_{\mathrm{OFF}}$ (blue, λ_{ex} = 380 nm) in 50% aqueous CH_3CN. The hump close to 760 nm in the emission corresponds to the Raman line.

formation of small aryl units.[10e] Clearly, the pendant anthracene chromophore is dearomatized (destroyed), while the remaining absorptions persist similar to those of the corresponding *alkyl*-functionalized Ru^{2+} and Re^+ chromophores, vide infra. The UV–vis absorption changes were utilized to determine the photogeneration quantum yield Φ_{pdt}[10a] for $\mathbf{1}_{\mathrm{ON}}$ (Φ_{pdt} = 0.018) and $\mathbf{2}_{\mathrm{ON}}$ (Φ_{pdt} = 0.022) (Chart 1) in 50% aqueous CH_3CN with reference to the photohydration of 2-(anthracen-9-yl)phenol (Φ_{pdt} = 0.09 in D_2O+CH_3CN).[10e]

Luminescence spectra recorded after about 90 min of photolysis already exhibit broad and unstructured peaks (Figure 6) at $\lambda_{\max}$ = 626 and 616 nm that are characteristic ^{3}MLCT emission for Ru^{2+} and Re^+ complexes, respectively.[5,17] To reach maximum PL intensity at saturation level (no further enhancement or loss), however, 18 h of photoexcitation are required.[24] The growth of ^{3}MLCT emission intensity with increasing destruction of the appended organic chromophore proves that the latter is responsible for the nonemissive nature of the inorganic luminophore in $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$.[5−9] Luminescence excitation spectra of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ were measured after 18 h of photolysis monitoring both anthracene- and MLCT based emissions. While the MLCT-based transition was clearly discernible between 400 and 460 nm, anthracene-based transitions were not detected in the spectra (Supporting Information, Figure S4) indicating that exclusively anthracene had undergone photodehydration.

Upon preparative photolysis, $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ transformed into the hydrated analogues $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$, as clearly supported by mass and elemental analysis results. Throughout photolysis, the inorganic complex of both compounds was not affected because its MLCT absorption band remained unaltered. Moreover, optical properties of $\mathbf{1}_{\mathrm{ON}}$, $\mathbf{2}_{\mathrm{ON}}$ are rather different from those of $\mathbf{1}_{\mathrm{OFF}}$, $\mathbf{2}_{\mathrm{OFF}}$ as apparent from their UV–vis and PL data. The

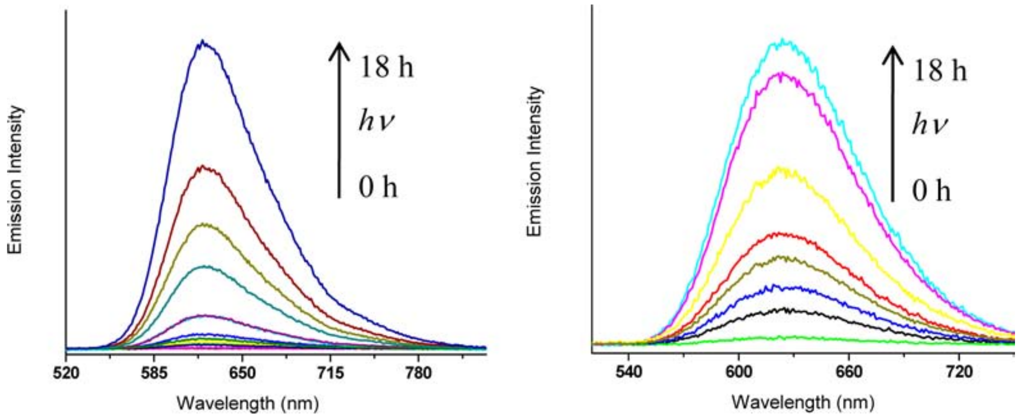


Figure 7. Luminescence spectra of $\mathbf{1}_{OFF}$→$\mathbf{1}_{ON}$ (left), and $\mathbf{2}_{OFF}$→$\mathbf{2}_{ON}$ (right) measured at 2 h intervals during photodearomatization (λ_{ex} = 355 ± 5 nm). Notice that the MLCT emission intensity increases upon irradiation.

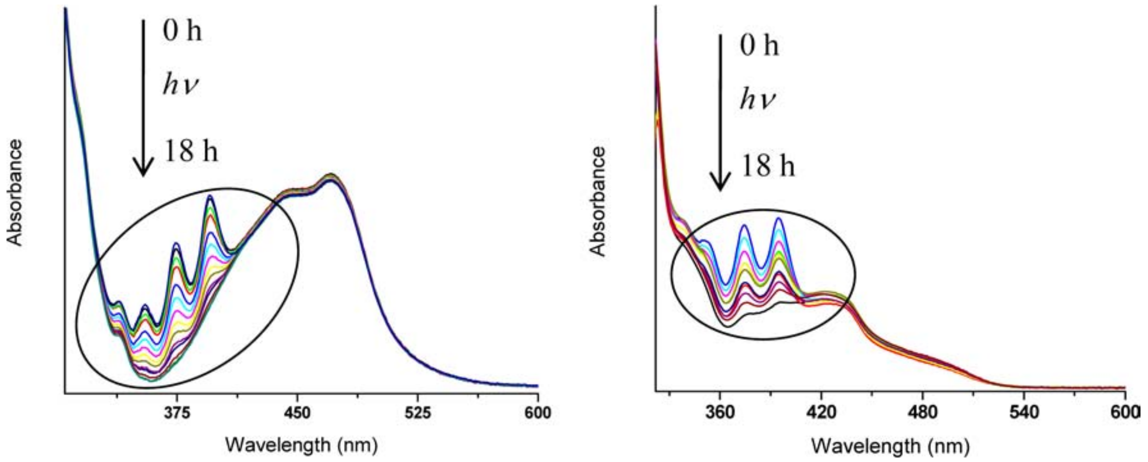


Figure 8. Absorption spectra of $\mathbf{1}_{OFF}$→$\mathbf{1}_{ON}$ (left), and $\mathbf{2}_{OFF}$→$\mathbf{2}_{ON}$ (right) measured at 2 h intervals during photodearomatization (λ_{ex} = 355 ± 5 nm). Notice that the absorption for the 2-(anthracen-9-yl)-4-methylphenol residue decreases during irradiation.

photophysical characteristics of $\mathbf{1}_{ON}$ and $\mathbf{2}_{ON}$ (Table 1) are actually similar to those of *alkyl*-functionalized metal complexes, such as $[Ru(phen)_2L]^{2+}$ with L = 2-(1-methylbenzimidazol-2-yl)pyridine[26] ($\lambda_{max}{}^{abs}$ = 468 nm, $\lambda_{max}{}^{PL}$ = 619 nm) and $[Re(CO)_3(Cl)L]$ with L = 2-(1-ethylbenzimidazol-2-yl)pyridine[27] ($\lambda_{max}{}^{abs}$ = 413 nm, $\lambda_{max}{}^{PL}$ = 616 nm), respectively.

Photoinduced and Thermal Switching of Luminescence. To study the suitability of **1** and **2** to act as reversible ON and OFF luminescence switches, their ON state $\mathbf{1}_{ON}$/$\mathbf{2}_{ON}$ was produced photochemically and reversed thermally to the OFF state $\mathbf{1}_{OFF}$/$\mathbf{2}_{OFF}$. Clean thermal switching could be achieved by heating $\mathbf{1}_{ON}$ and $\mathbf{2}_{ON}$ at 80−90 °C, as evident from NMR (Supporting Information, Figures S30 and S31) and quantum yields (Supporting Information, Table S1).

OFF → ON → OFF switching was monitored by PL and UV−vis studies taking spectra at 2 h intervals (Figures 7 and 8). Upon constant irradiation of $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ using either a xenon lamp or a Rayonet photoreactor (λ_{ex} = 355 ± 5), the intensity of the ^{3}MLCT emission increased by 120−150 fold (Figure 7) due to formation of $\mathbf{1}_{ON}$/$\mathbf{2}_{ON}$ (Chart 1). After about 18 h of irradiation, no further PL intensity variation was noticed. At this point, emission quantum yields were determined by using $[Ru(bpy)_3]^{2+}$ as a standard in aerated water (Φ = 0.028)[28] yielding Φ = 0.0142 and 0.0031 for $\mathbf{1}_{ON}$ and $\mathbf{2}_{ON}$, respectively. It is worthy of mention that both PL emission wavelengths and quantum yields of $\mathbf{1}_{ON}$ and $\mathbf{2}_{ON}$ are comparable to those of the corresponding *alkyl*-substituted metal complexes, such as $[Ru(phen)_2L]^{2+}$ with L = 2-(1-methylbenzimidazol-2-yl)pyridine, Φ = 0.017[26] and $[Re(CO)_3ClL]$ with L = 2-(1-ethylbenzimidazol-2-yl)pyridine, Φ = 0.002.[27] The determined PL quantum yields are in agreement with NMR findings that $\mathbf{1}_{OFF}$/$\mathbf{2}_{OFF}$ transformed fairly into $\mathbf{1}_{ON}$/$\mathbf{2}_{ON}$. In OFF → ON photoswitching, the absorption bands between 350 and 400 nm belonging to the 2-(anthracen-9-yl)-4-methylphenol residue completely disappeared after 18 h of excitation (Figure 8). Thus, this moiety is entirely dearomatized after photolysis.[10]

Aryl carbinols are unstable and undergo dehydration in acidic medium,[29] as do 9-hydroxy-9-aryl-10-hydroanthracenes that form 9-arylanthracenes.[30] As a result, $\mathbf{1}_{ON}$/$\mathbf{2}_{ON}$ were transformed into $\mathbf{1}_{OFF}$/$\mathbf{2}_{OFF}$ by dehydration. Full conversion was observed at 80−90 °C within 4 h, while in the presence of desiccants, such as molecular sieves or acidic alumina, the transformation was even accomplished at 40−50 °C within 2.5−3 h. Both $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$, as obtained by dehydration, were characterized by NMR and mass analysis. As expected, the ^{1}H and ^{13}C NMR signals of the dehydrated compounds were found to be identical to those of $\mathbf{1}_{OFF}$ and $\mathbf{2}_{OFF}$ prepared independently (Scheme 1 and Supporting Information, Figures S30 and S31).

The thermal dehydration of $\mathbf{1}_{ON}$/$\mathbf{2}_{ON}$ in dry CH_3CN without any desiccant was monitored over time by absorption and PL

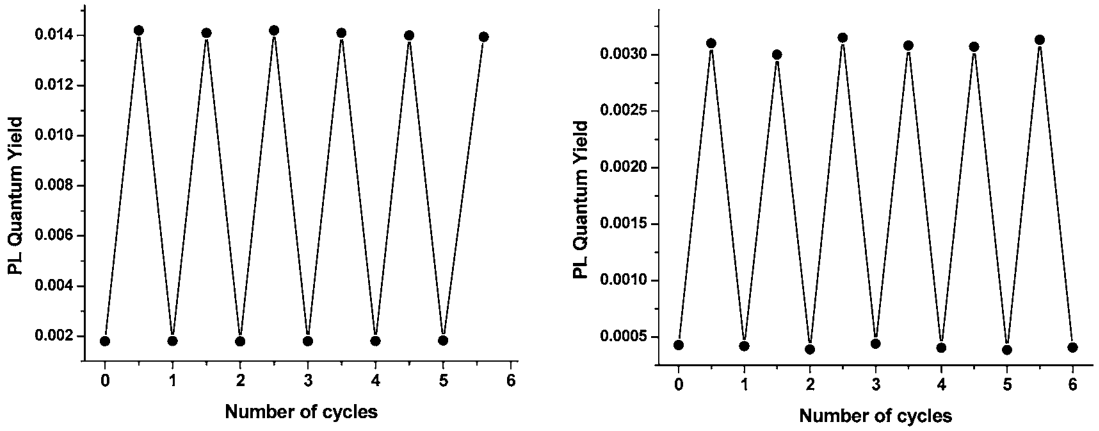
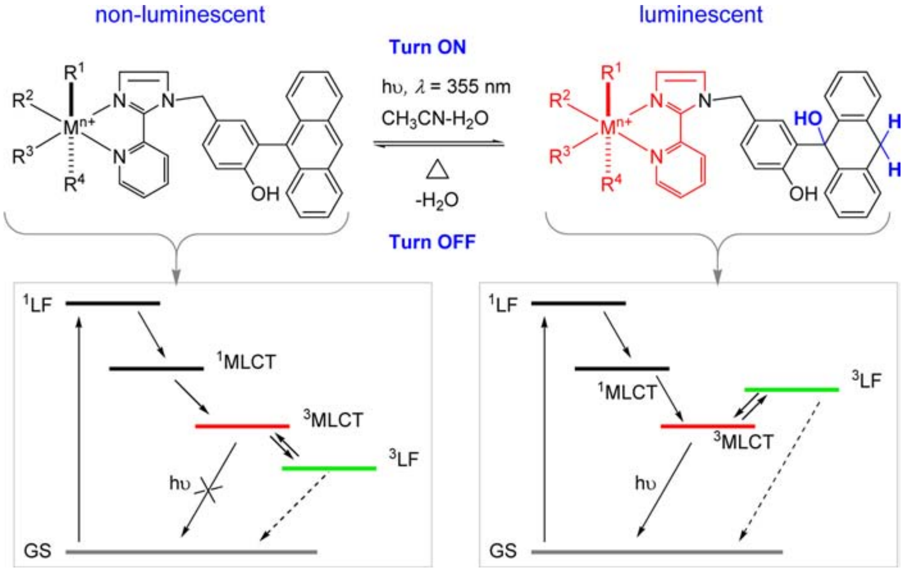


Figure 9. Reversible switching behavior of $\mathbf{1}_{\mathrm{OFF}}$ to $\mathbf{1}_{\mathrm{ON}}$ ($\mathbf{1}_{\mathrm{OFF}}\leftrightarrow\mathbf{1}_{\mathrm{ON}}$, left) and $\mathbf{2}_{\mathrm{OFF}}$ to $\mathbf{2}_{\mathrm{ON}}$ ($\mathbf{2}_{\mathrm{OFF}}\leftrightarrow\mathbf{2}_{\mathrm{ON}}$, right) or vice versa, during photoirradiation followed by thermal dehydration experiments. $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ at start of cycle 1 were produced by thermal dehydration of $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$.

Scheme 2. Proposed Mechanism of Switching in Dyads 1 and 2[a]



[a] Notice that the triplet state energy and conjugation of the organic pendant changes during photodearomatization and thermal aromatization (LF − ligand field of 2-(anthracen-9-yl)-4-methylphenol unit).

studies. At 80−90 °C the initial PL intensity of solutions of $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$ commenced to bleach after 20 min and complete loss of emission was realized after 4 h. At this time, the ^{3}MLCT emissions of $\mathbf{1}_{\mathrm{ON}}$ at 550−750 nm and of $\mathbf{2}_{\mathrm{ON}}$ at 550−700 nm had disappeared substantially and their quantum yield values had fallen to $<10^{-3}$ (Supporting Information, Table S1). The half-life of the thermal dehydration of $\mathbf{1}_{\mathrm{ON}}$ to $\mathbf{1}_{\mathrm{OFF}}$ ($t_{1/2}$ = 154 min) and $\mathbf{2}_{\mathrm{ON}}$ to $\mathbf{2}_{\mathrm{OFF}}$ ($t_{1/2}$ = 147 min) was determined at 80 °C by monitoring the decreasing PL intensity over time (Supporting Information, Figures S32 and S33). In the absorption channel, the signals for 2-(anthracen-9-yl)-4-methylphenol fully recovered with ε being comparable to that of fresh $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$. Quantitative transformation to $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ was equally corroborated from NMR (Supporting Information, Figures S30 and S31). Perceptibly, the spectral changes observed during thermal rearomatization, ON → OFF, were reversing those of the initial photodearomatization, OFF → ON, shown in Figures 7 and 8.

To check for multiple reversible switching, we performed the photodearomatization and thermal rearomatization repeatedly and monitored its course over 5 cycles (Figure 9). The result shows that conversion of $\mathbf{1}_{\mathrm{OFF}}\rightarrow\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{OFF}}\rightarrow\mathbf{2}_{\mathrm{ON}}$ and vice versa takes place cleanly and without substantial degradation (Supporting Information, Table S1 and Figures S30 and S31).

■ DISCUSSION

Mechanism of Luminescence Switching. As mentioned in the introduction, various anthracene derivatives have been described to quench the MLCT emissions of appended transition metal complexes, including those of Ru^{2+} and Re^{+} luminophores, via energy transfer (Supporting Information, Charts S1 and S2).[1a,b,4f,5−9] The PL quantum yields of these dyads were found to be in the order of 10^{-3} to 10^{-4} at room temperature,[6,31] with quantum yields increasing >100 fold after oxidation of anthracene residue with either $^1O_2$ or H_2O_2.[5,7] Photophysical studies on these multichromophoric systems,[32] in particular those with anthracene or perylene decorated transition metal complexes, reveal no absorption for the inorganic subunit in the transient absorption spectra. Rather they exhibit an intense absorption corresponding to the $^3\pi-\pi^*$

state of the pendant organic substituent. The sum of these findings indicates that the ^{3}MLCT state has been effectively quenched via energy transfer to the lower-lying nonradiative $^3\pi-\pi^*$ state of the attached organic unit.[7,32]

Based on these results and the optical properties of luminescent switches $\mathbf{1}_{\mathrm{OFF}}$/$\mathbf{2}_{\mathrm{OFF}}$ and their photoproducts $\mathbf{1}_{\mathrm{ON}}$/$\mathbf{2}_{\mathrm{ON}}$, we propose a possible working mechanism and energy level change during photodearomatization and thermal aromatization in Scheme 2. A key element of our mechanistic proposal is that the quenching process $^3\mathrm{MLCT}\rightarrow{}^3\pi-\pi^*$ is absent, when the pendant 2-(anthracen-9-yl)-4-methylphenol in $\mathbf{1}_{\mathrm{OFF}}$/$\mathbf{2}_{\mathrm{OFF}}$ has undergone ESIPT photohydration to $\mathbf{1}_{\mathrm{ON}}$/$\mathbf{2}_{\mathrm{ON}}$.

Generalizations about the Functional Behavior of 1 and 2. The energy levels of anthracene and its derivatives can be modulated reversibly by different reactions, such as oxidation and reduction,[3k,33] cycloaddition and retro-cycloaddition,[34] ring closing and opening,[35] hydration and dehydration,[10] *etc.*[23] Among oxidation and reduction, cycloaddition and retro-cycloaddition, reactions of anthracene have been extensively employed in the development of molecular machines, sensors, switches, and so on.[1,36] However, the concept of hydration and dehydration at the anthracene core has not been explored practically for molecular materials.[1] This omission may be due to the essential need of an aqueous medium for hydration, where many compounds are either unstable or insoluble. To the best of our knowledge, we herein present the first example of a luminescent switch that is controlled by hydration and/or dehydration. Hybrids $\mathbf{1}_{\mathrm{OFF}}$/$\mathbf{2}_{\mathrm{OFF}}$ and $\mathbf{1}_{\mathrm{ON}}$/$\mathbf{2}_{\mathrm{ON}}$ are nicely soluble in aqueous medium and satisfy the basic requirements of molecular switches as their functional behavior is tuned in response to external stimuli, that is, light and heat. In addition, they undergo switching, that is, readout (hydration) and erase (dehydration), quantitatively (by Φ_{PL} and NMR) and rather rapidly, when compared to how analogue hybrid switches work in nonaqueous medium.[1,4,5,8,9] Complete photohydration of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ happens within 18 h as judged by full MLCT emission gain, whereas analogue systems operating on either cycloaddition or oxidation of anthracenes require 24−48 h.[7−9,33] Likewise, luminescence is fully erased by thermal dehydration of $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$ after 4 h, while more than 48 h are required for partial retro-cycloaddition of anthracenyl adducts.[8,9,34]

CONCLUSIONS

Readout/write behavior of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ was readily tuned by photohydration involving dearomatization using ESIPT photochemistry, and *erase* by thermal dehydration of $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$ at moderate temperature. *Readout/write* cycles were run five times without fatigue. The ready accessibility, complete reversibility and the water-mediated functionality of $\mathbf{1}_{\mathrm{OFF}}$ and $\mathbf{2}_{\mathrm{OFF}}$ may warrant the exploration of future applications in biological fluids and settings.

EXPERIMENTAL SECTION

General Aspects. All reactions were performed under a nitrogen gas atmosphere in oven-dried glassware. The solvents tetrahydrofuran (THF) and toluene were freshly distilled over sodium, whereas CH_2Cl_2 and CH_3CN were distilled over CaH_2 prior to use. All reactions were monitored by precoated analytical thin layer chromatography (TLC) on silica gel/alumina. Column chromatography was conducted with silica gel (60−120 mesh). All commercial chemicals were used as received. All intermediates and metal complexes proved to be air- and moisture-stable, which allowed all measurements to be done at ambient conditions unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in deuterated solvents. Chemical shifts are reported in δ-scale (ppm) and are referenced to residual protiated solvent. Infrared spectra were recorded on a Varian 1000 FT-IR instrument, and the ESI mass spectra were recorded on a Thermo-Quest LCQ Deca instrument. Elemental analysis was measured using a EA 3000 CHNS.

UV−vis absorption spectra were recorded on a Varian Cary 100 Bio-UV/Visible spectrometer either in CH_3CN or 50:50 aqueous CH_3CN-water. PL spectra and PL quantum yields (Φ_{PL}) and excitation spectra were measured on a Varian Cary Eclipse Fluorescence Spectrophotometer with excitation and emission slits set to either 2.5 or 5 nm. PL quantum yields (Φ_{PL}) were determined using $[\mathrm{Ru(bpy)_3}]^{2+}$ as a standard (Φ = 0.028, λ_{exc} = 450 nm)[28] in aerated CH_3CN-water solution. The following equation was used for the calculation of Φ_{PL} for $\mathbf{1}_{\mathrm{ON}}$ and $\mathbf{2}_{\mathrm{ON}}$:

$$\Phi_{\mathrm{u}} = \Phi_{\mathrm{s}}(I_{\mathrm{u}}/I_{\mathrm{s}})(A_{\mathrm{s}}/A_{\mathrm{u}})(\eta_{\mathrm{u}}/\eta_{\mathrm{s}})^2$$

with the subscripts "s" and "u" referring to standard and unknown samples, A_{u} and A_{s} to absorbances at the excitation wavelength, I_{u} and I_{s} to the integrated emission intensities (i.e., areas under the emission curves), and η_{u} and η_{s} to the refractive indexes of the corresponding solutions.

General Procedure for the Photohydration.[10] A solution of either ligand **3** or $\mathbf{1}_{\mathrm{OFF}}$ or $\mathbf{2}_{\mathrm{OFF}}$ (ca. 20 mg) in 4−5 mL of deionized water-CH_3CN (50:50) was irradiated with a Xenon lamp or in a preparative photoreactor (λ_{ex} = 355 ± 5) at room temperature. Progress of the reaction was monitored by UV−vis and PL analysis. After completion of the reaction (no further change in intensity and/or shape of a profile), the volatiles were removed under vacuum at room temperature. The resultant semisolid was dissolved in methanol and passed through a short pad of Celite column yielding the hydrated products **4** or $\mathbf{1}_{\mathrm{ON}}$ or $\mathbf{2}_{\mathrm{ON}}$ in near quantitative yields (>93−97%). In case of **4** CH_2Cl_2 was used for purification instead of methanol.

General Procedure for Product Quantum Yield (Φ_{pdt}) Measurements.[10a,e] Solutions of substrate, either ligand **3** or $\mathbf{1}_{\mathrm{OFF}}$ or $\mathbf{2}_{\mathrm{OFF}}$, in deionized water−$CH_3CN$ (50:50, v/v) and of the standard 2-(anthracen-9-yl)phenol, in 4 M D_2O−CH_3CN solution, were placed in two separate quartz cuvettes (3.0 mL). The solutions were purged with N_2 gas over 10 min, then their optical density (OD) was adjusted to the same value at 350 nm. Subsequently, solutions were irradiated with a Xenon lamp (λ_{ex} = 355 ± 5) for about 3.0 h. Thereafter, the OD for both analyte and standard was measured again, and the loss of OD vs irradiation time was followed and compared with that of the unphotolyzed solution. The value of quantum yield was estimated from the equation described in the literature.[10a]

$$\Phi_{\mathrm{pdt}} = \Delta A_{\lambda}/10^3\varepsilon_{\lambda}\Delta I_{\mathrm{a}}$$

ΔA_{λ} is the loss of OD at 350 nm, ε_{λ} is the extinction coefficient at excitation wavelength, and ΔI_{a} is the number of photons absorbed per unit volume during the irradiation.

General Procedure for Thermal Dehydration. A solution of $\mathbf{1}_{\mathrm{ON}}$ or $\mathbf{2}_{\mathrm{ON}}$ (ca. 20 mg) in 5 mL of acetonitrile was heated at 80−90 °C until complete dehydration was seen (4 h). The progress of the reaction was monitored by UV−vis and PL analysis. After completion of the reaction, the volatiles were removed under vacuum. The resultant solid material was dissolved in methanol and passed through a short pad of Celite column yielding the dehydrated products $\mathbf{1}_{\mathrm{OFF}}$ or $\mathbf{2}_{\mathrm{OFF}}$ in near quantitative yields (>92−97%).

Preparation of 9-Anthraceneboronic Acid.[37] To a solution of 9-bromoanthracene (1.9 g, 7.5 mmol) in THF (50 mL) kept at −50 to −60 °C (low temperature maintained by using acetone-liquid nitrogen bath) was added nBuLi (11.0 mmol) dropwise over 30 min. The resultant red colored solution was stirred for 1 h at the same temperature, subsequently trimethyl borate (11.0 mmol) was added slowly. The reaction mixture was brought to room temperature over a period of 2 h, then aqueous HCl (5 mL) was added. The volatiles were removed and the organic material was extracted with ethyl acetate. The combined extract was dried over Na_2SO_4 and evaporated. The pure product was obtained after filtration over a short pad of silica-gel using 30% ethyl acetate in hexane, followed by recrystallization from ethyl acetate and hexane furnishing 9-anthraceneboronic acid as a pale yellow solid (1.2 g, 70%): mp 214−219 °C (mp 217 °C);[37] R_f 0.41 in 50% ethyl acetate in hexane; ^1H NMR (400 MHz, acetone-d_6) δ 7.47−7.50 (m, 4H, 2-, 3-H), 7.86 (s, 2H, −OH), 8.03−8.06 (m, 2H, 4-H), 8.12−8.14 (m, 2H, 1-H), 8.49 (s, 1H, 5-H); ^{13}C NMR (100 MHz, acetone-d_6) δ 111.5, 126.8, 126.9, 128.4, 130.4, 130.9, 133.2, 135.3.

Preparation of 3-(Anthracen-9-yl)-4-methoxybenzaldehyde.[38] 9-Anthraceneboronic acid (1.0 g, 4.5 mmol), 2-bromo-4-anisaldehyde (1.2 g, 5.4 mmol), and $[Pd(PPh_3)_4]$ (0.26 g, 5.0 mol %) were introduced into an initially oven-dried pressure tube under N_2. To this mixture were added THF (30 mL) and saturated aqueous K_2CO_3 solution (10 mL). The reaction mixture was refluxed at 85−90 °C for 36 h and then cooled to room temperature. The contents were extracted with CH_2Cl_2, dried over Na_2SO_4, and the solvent was evaporated. The resultant material was purified by silica gel column chromatography using 25% CH_2Cl_2 in hexane, yielding 3-(anthracen-9-yl)-4-methoxybenzaldehyde as a colorless solid (0.59 g, 43%): mp 161−164 °C (mp 164 °C);[38] R_f 0.16 in 2.5% ethyl acetate in hexane; ^1H NMR (400 MHz, CD_2Cl_2) δ 3.93 (s, 3H, 9-H), 7.01 (d, J = 2.4 Hz, 1H, 8-H), 7.39−7.41 (m, 2H, 6-, 7-H), 7.49−7.53 (m, 2H, 3-H), 7.58−7.62 (m, 2H, 2-H), 8.00 (d, J = 8.8 Hz, 2H, 4-H), 8.45 (s, 1H, 5-H), 8.49 (d, J = 9.2 Hz, 2H, 1-H), 9.79 (s, 1H, 10-H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 56.1, 108.9, 114.2, 121.9, 125.6, 126.8, 127.1, 127.2, 127.3, 128.5, 129.9, 130.4, 132.1, 147.2, 151.5, 190.5.

Preparation of 2-(Anthracen-9-yl)-4-(hydroxymethyl)-phenol. To a solution of 3-(anthracen-9-yl)-4-methoxybenzaldehyde (0.55 g, 1.8 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added dropwise 1.0 M BBr_3 in CH_2Cl_2 (0.7 mL) under N_2 gas atmosphere. The purple color reaction mixture was stirred overnight, and subsequently it was quenched with ethanol. The volatiles were removed under vacuum yielding a semisolid that was taken as such to the $NaBH_4$ reduction. About 20−25 mL of ethanol and $NaBH_4$ (0.41 g, 1.1 mmol) were added to the contents. The resultant yellow solution was stirred at room temperature for about 1 h. Thereafter volatiles were removed, and the organic material was extracted with ethyl acetate. The combined extract was dried over Na_2SO_4 and evaporated. The pure product was obtained after chromatography over silica gel using 30% ethyl acetate in hexane, followed by recrystallization from ethyl acetate and hexane furnishing 2-(anthracen-9-yl)-4-(hydroxymethyl)phenol as a colorless solid (0.41 g, 74%): mp 252 °C dec.; R_f 0.21 in 25% ethyl acetate in hexane; ^1H NMR (400 MHz, CD_2Cl_2) δ 1.90 (s, 1H, 17-H), 5.61 (s, 2H, 10-H), 7.46−7.50 (m, 2H, 6-, 7-H), 7.53−7.61 (m, 4H, 2-, 3-H), 7.97 (d, J = 2.4 Hz, 1H, 8-H), 8.02 (d, J = 8.8 Hz, 2H, 4-H), 8.39 (d, J = 9.2 Hz, 2H, 1-H), 8.46 (s, 1H, 5-H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 57.2, 113.2, 121.5, 124.1, 125.2, 126.4, 128.2, 128.6, 129.1, 130.3, 131.5, 131.6, 136.3, 136.5; Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.87; H, 5.38.

Preparation of 2-(Imidazol-2-yl)pyridine.[15] To a solution of pyridine-2-carboxaldehyde (20.0 g, 187 mmol) and 27 mL of 40% aqueous glyoxal in 40 mL of ethanol at 0 °C was added at once 64 mL of cold aqueous NH_3 (30%). The mixture was stirred at 0 °C for 1 h, brought to room temperature, and stirred for another 1 h. Subsequently, all volatiles were removed and extracted with CH_2Cl_2. The combined extract was dried over Na_2SO_4 and evaporated. The resultant dark brown oil was distilled at 180 °C under vacuum. The colorless to pale yellow oil solidified on standing (8.0 g, 30%): mp 133−136 °C (mp 135 °C)[15]; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.16 (s, 2H, 11-, 12-H), 7.25 (dd, J = 4.0 Hz, J = 1.2 Hz, 1H, 14-H), 7.78 (dd, J = 2.0 Hz, J = 1.6 Hz, 1H, 15-H), 8.20 (d, J = 8.0 Hz, 1H, 16-H), 8.50 (d, J = 4.8 Hz, 1H, 13-H), 11.86 (s, 1H, 18-H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 120.0, 120.1, 123.1, 137.3, 146.4, 148.7, 148.9, 149.0.

Preparation of 3.[14] 2-(Anthracen-9-yl)-4-(hydroxymethyl)phenol (0.40 g, 1.3 mmol) and 2-(imidazol-2-yl)pyridine (0.38 g, 2.7 mmol) were mixed thoroughly with a spatula and heated at 120 °C for 1 h, later at 140 °C for further 6 h. The yellow semisolid was treated with 80:20 hexane-CH_2Cl_2 to remove unreacted starting precursors. The insoluble material was isolated by filtration and further purified by silica gel column chromatography using 10−30% methanol in CH_2Cl_2 yielding **3** as a faint yellow solid (0.35 g, 62%): mp 141−146 °C; R_f 0.13 in 20% methanol in CH_2Cl_2; IR (KBr cm^{-1}) 3463, 3322, 2951, 2934, 2880, 2751, 2671, 1366, 1351, 1332, 1288, 1269, 1226, 1197, 1107, 1097, 958, 895, 878, 871, 852, 844; ^1H NMR (400 MHz, CD_2Cl_2) δ 5.89 (s, 2H, 10-H), 7.02 (d, J = 1.4 Hz, 1H, 11-H), 7.09−7.17 (m, 3H, 6-, 7-, 12-H), 7.20 (dd, J = 3.6 Hz, J = 1.2 Hz, 1H, 14-H), 7.33−7.37 (m, 2H, 15-, 8-H), 7.58 (t, J = 7.2 Hz, 2H, 3-H), 7.69−7.75 (m, 3H, 2-, 9-H), 8.08 (d, J = 8.8 Hz, 2H, 4-H), 8.17 (d, J = 8.0 Hz, 1H, 16-H), 8.37 (d, J = 7.6 Hz, 2H, 1-H), 8.49 (d, J = 5.2 Hz, 1H, 13-H), 8.68 (s, 1H, 5-H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 50.9, 105.5, 117.1, 122.6, 122.7, 123.5, 125.2, 126.0, 126.4, 128.9, 129.0, 129.1, 130.2, 130.3, 130.5, 130.7, 132.9, 133.3, 136.7, 140.8, 144.5, 148.2, 150.7; ESI-MS m/z (%) 428.2 (100) $[M+1]^+$. Anal. Calcd for $C_{29}H_{21}N_3O$: C, 81.48; H, 4.95; N, 9.83. Found: C, 81.22; H, 4.92; N, 9.67.

Photolysis of 3 in CH_3CN-Water. Photolysis was performed by following the general procedure described in the photohydration section. The photoproduct **4** was obtained in 94−95% yield: mp 121−125 °C; R_f 0.14 in 20% methanol in CH_2Cl_2; IR (KBr cm^{-1}) 3510, 3327, 3057, 3045, 2969, 2774, 1635, 1602, 1591, 1536, 1516, 1493, 1453, 1421, 1397, 1322, 1284, 1265, 1239, 1162, 1154, 1039, 1009, 966, 915, 907, 841; ^1H NMR (400 MHz, CD_2Cl_2) δ 3.96 (s, 2H, 5-H), 5.90 (s, 2H, 10-H), 7.02 (d, J = 1.2 Hz, 1H, 11-H), 7.10−7.22 (m, 9H, 2-, 3-, 4-, 6-, 7-, 12-H), 7.25−7.30 (m, 3H, 1-, 9-H), 7.34−7.38 (m, 2H, 15-, 8-H), 7.74 (dd, J = 6.0 Hz, J = 1.6 Hz, 1H, 14-H), 8.18 (d, J = 8.0 Hz, 1H, 16-H), 8.50 (d, J = 4.4 Hz, 1H, 13-H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 36.2, 52.2, 81.1, 123.8, 124.2, 124.4, 125.9, 126.4, 127.6, 128.0, 128.7, 130.5, 130.6, 132.0, 132.1, 132.3, 138.6, 138.8, 140.5, 143.4, 145.8, 150.0, 152.7; ESI-MS m/z (%) 445.8 (100) $[M+1]^+$. Anal. Calcd for $C_{29}H_{23}N_3O_2$: C, 78.18; H, 5.2; N, 9.43. Found: C, 78.31; H, 5.19; N, 9.46.

Photolysis of 3 in CH_3OH-Water. Photolysis was performed by following the general procedure described in the photohydration section The photoproduct **5** was obtained in 93−95% yield: mp 119−122 °C; R_f 0.16 in 20% methanol in CH_2Cl_2; IR (KBr cm^{-1}) 3494, 3380, 3317, 3091, 2996, 2977, 2964, 2855, 2653, 2624, 2611, 1623, 1603, 1581, 1537, 1489, 1453, 1434, 1385, 1370, 1324, 1305, 1261, 1230, 1199, 1157, 1041, 1030, 1019; ^1H NMR (400 MHz, CD_2Cl_2) δ 3.57 (s, 3H, 21-H), 3.94 (s, 2H, 5-H), 5.89 (s, 2H, 10-H), 7.01 (d, J = 1.2 Hz, 1H, 11-H), 7.09−7.20 (m, 9H, 2-, 3-, 4-, 6-, 7-, 12-H), 7.24−7.27 (m, 3H, 1-, 9-H), 7.33−7.37 (m, 2H, 15-, 8-H), 7.72 (dd, J = 5.6 Hz, J = 1.6 Hz, 1H, 14-H), 8.17 (d, J = 8.0 Hz, 1H, 16-H), 8.50 (d, J = 4.4 Hz, 1H, 13-H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 37.0, 50.9, 70.4, 119.8, 122.5, 122.6, 122.7, 123.6, 125.1, 126.0, 126.7, 126.8, 128.9, 130.2, 130.3, 130.5, 136.7, 140.7, 140.8, 141.7, 143.4, 144.5, 148.2, 150.7; ESI-MS m/z (%) 459.6 (100) $[M+1]^+$. Anal. Calcd for $C_{30}H_{25}N_3O_2$: C, 78.41; H, 5.48; N, 9.14. Found: C, 78.39; H, 5.47; N, 9.15.

Preparation of 1_{OFF}.[11] A suspension of $[Ru(phen)_2]Cl_2$ (0.12 g, 0.21 mmol) and ligand **3** (0.10 g, 0.21 mmol) in 40 mL of 20% aqueous ethanol was refluxed under N_2 for 8 h. After this period, the wine-red solution was concentrated to about 5−7 mL, then acetone (20 mL) was added. The resultant red precipitate was isolated by filtration and washed with a small portion of cold acetone. The pure product was obtained after filtration over a short pad of silica-gel using ethanol followed by 10−25% ammonium hexafluorophosphate in methanol to yield 0.21 g (55%): IR (KBr, cm^{-1}) 3470, 3089, 2864, 1608, 1596, 1561, 1514, 1428, 1263, 1116, 954, 840, 733; ^1H NMR (400 MHz, CD_3OD) δ 5.89 (s, 2H, 10-H), 7.23−7.29 (m, 2H, 6-, 7-H), 7.40−7.51 (m, 6H, 2-, 3-, 8-, 9-H), 7.64 (dd, J = 4.0 Hz, J = 0.8 Hz, 1H, 14-H), 7.73 (d, J = 2.0 Hz, 1H, 11-H), 7.78 (d, J = 2.0 Hz, 1H, 12-H), 7.91 (d, J = 8.4 Hz, 2H, 4-H), 7.96−8.01 (m, 3H, 1-, 16-H), 8.05−8.12 (m, 5H, 15-, 19-H), 8.16 (s, 4H, 17-H), 8.35 (s, 1H, 5-H), 8.81−8.83 (m, 1H, 13-H), 8.89 (dd, J = 6.8 Hz, J = 1.6 Hz, 4H, 18-H), 9.19 (dd, J = 3.6 Hz, J = 1.6 Hz, 4H, 20-H); ^{13}C NMR (100 MHz, CH_3OD + CD_3COCD_3, 50:50 v/v) δ 57.7, 101.5, 114.2, 115.4, 120.3, 123.2, 123.9, 126.3, 126.8, 127.0, 127.7, 129.2, 129.4, 130.0, 130.6, 131.1, 131.6, 132.2, 133.4, 133.8, 135.5, 138.1, 138.3, 141.2, 142.6, 143.6, 147.6, 149.8, 152.3; ESI-MS *m*/*z* (%) 924.4 (100) [M−Cl]$^+$. Anal. Calcd for $C_{53}H_{37}N_7OF_{12}P_2Ru$: C, 54.00; H, 3.16; N, 8.32. Found: C, 53.93; H, 3.12; N, 8.31.

Preparation of $\mathbf{2}_{\mathrm{OFF}}$.[6] A suspension of [Re(CO)$_5$Cl] (0.15 g, 0.42 mmol) and ligand **3** (0.17 g, 0.42 mmol) in 30 mL of degassed toluene was refluxed under N_2 for 24 h. The reaction mixture was cooled to room temperature, and the solid was isolated by filtration. The lemon yellow solid was recrystallized in 30% CH_2Cl_2 in hexane twice to yield 0.22 g (72%): IR (KBr cm^{-1}) 3456, 2987, 2924, 2821, 2693, 2029, 1919, 1493, 1322, 1286, 1250, 1147, 1065, 956, 902, 883, 866, 851; ^{1}H NMR (400 MHz, CD_3OD) δ 5.87 (s, 2H, 10-H), 7.25−7.26 (m, 2H, 6-, 7-H), 7.47−7.58 (m, 6H, 2-, 3-, 8-, 9-H), 7.63 (dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 1H, 14-H), 7.70 (d, *J* = 2.0 Hz, 1H, 11-H), 7.76 (d, *J* = 2.0 Hz, 1H, 12-H), 7.95 (d, *J* = 8.0 Hz, 1H, 16-H), 8.04 (d, *J* = 2.0 Hz, 1H, 15-H), 8.05−8.12 (m, 4H, 1-, 4-H), 8.58 (s, 1H, 5-H), 8.80 (d, *J* = 3.6 Hz, 1H, 13-H); ^{13}C NMR (100 MHz, CD_3OD) δ 52.9, 123.9, 125.6, 126.2, 127.1, 127.2, 127.8, 127.9, 128.0, 128.5, 129.9, 131.9, 132.1, 132.9, 135.3, 135.4, 138.6, 139.5, 139.6, 139.7, 144.1, 151.5, 181.2, 190.2; ESI-MS *m*/*z* (%) 700.8 (100) [M−Cl]$^+$. Anal. Calcd for $C_{32}H_{21}N_3O_4ClRe$: C, 52.42; H, 2.89; N, 5.73. Found: C, 52.41; H, 2.92; N, 5.74.

Preparation of $\mathbf{1}_{\mathrm{ON}}$. This compound was prepared starting from $\mathbf{1}_{\mathrm{OFF}}$ by following the general procedure described in the photohydration section (yield 95−97%): IR (KBr cm^{-1}) 3466, 3211, 3106, 3051, 2934, 2811, 1624, 1593, 1552, 1514, 1451, 1354, 1363, 1301, 1266, 1212, 1121, 1004, 940, 839; ^{1}H NMR (400 MHz, CD_3OD) δ 3.90 (s, 2H, 5-H), 5.92 (s, 2H, 10-H), 7.10−7.15 (m, 6H, 2-, 3-, 6-, COH-H), 7.20−7.31 (m, 5H, 1-, 4-, 7-H), 7.47 (d, *J* = 8.0 Hz, 1H, 8-H), 7.53 (s, 1H, 9-H), 7.66 (dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 1H, 14-H), 7.75 (d, *J* = 2.0 Hz, 1H, 11-H), 7.81 (d, *J* = 2.0 Hz, 1H, 12-H), 8.02 (d, *J* = 8.0 Hz, 1H, 16-H), 8.07−8.12 (m, 1H, 15-H), 8.16−8.19 (m, 4H, 19-H), 8.27 (s, 4H, 17-H), 8.84 (d, *J* = 4.0 Hz, 1H, 13-H), 8.98 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 4H, 18-H), 9.26 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 4H, 20-H); ^{13}C NMR (100 MHz, $CH_3OD+CD_3COCD_3$, 50:50 v/v) δ 38.3, 46.7, 101.4, 114.7, 120.2, 121.6, 123.8, 123.9, 127.0, 128.5, 128.6, 129.3, 129.4, 130.8, 131.4, 131.6, 132.4, 133.1, 133.4, 136.5, 141.6, 142.5, 143.3, 143.4, 145.1, 148.2, 150.0, 152.8; ESI-MS *m*/*z* (%) 943.7 (100) [M−Cl]$^+$. Anal. Calcd for $C_{53}H_{39}N_7O_2F_{12}P_2Ru$: C, 53.18; H, 3.28; N, 8.19. Found: C, 53.14; H, 3.17; N, 8.22.

Preparation of $\mathbf{2}_{\mathrm{ON}}$. This compound was prepared starting from $\mathbf{2}_{\mathrm{OFF}}$ by following the general procedure described in the photohydration section (yield 94−96%): IR (KBr cm^{-1}) 3398, 3289, 2992, 2911, 2877, 2032, 1915, 1603, 1512, 1401, 1374, 1281, 1254, 1211, 1054, 929, 876, 857; ^{1}H NMR (400 MHz, CD_3OD) δ 3.94 (s, 2H, 5-H), 5.91 (s, 2H, 10-H), 7.13−7.18 (m, 6H, 2-, 3-, 6-, COH-H), 7.22−7.28 (m, 5H, 1-, 4-, 7-H), 7.49 (d, *J* = 8.0 Hz, 1H, 8-H), 7.52 (s, 1H, 9-H), 7.65 (dd, *J* = 4.0 Hz, *J* = 1.2 Hz, 1H, 14-H), 7.72 (d, *J* = 2.0 Hz, 1H, 11-H), 7.78 (d, *J* = 2.0 Hz, 1H, 12-H), 7.99 (d, *J* = 7.2 Hz, 1H, 16-H), 8.06−8.11 (m, 1H, 15-H), 8.83 (d, *J* = 4.0 Hz, 1H, 13-H); ESI-MS *m*/*z* (%) 715.8 (100) [M−Cl]$^+$. Anal. Calcd for $C_{32}H_{23}N_3O_5ClRe$: C, 51.16; H, 3.09; N, 5.59. Found: C, 51.17; H, 3.12; N, 5.58.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional PL data, excitation spectra and NMR spectra for all intermediates and final compounds **ON** and **OFF**. 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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