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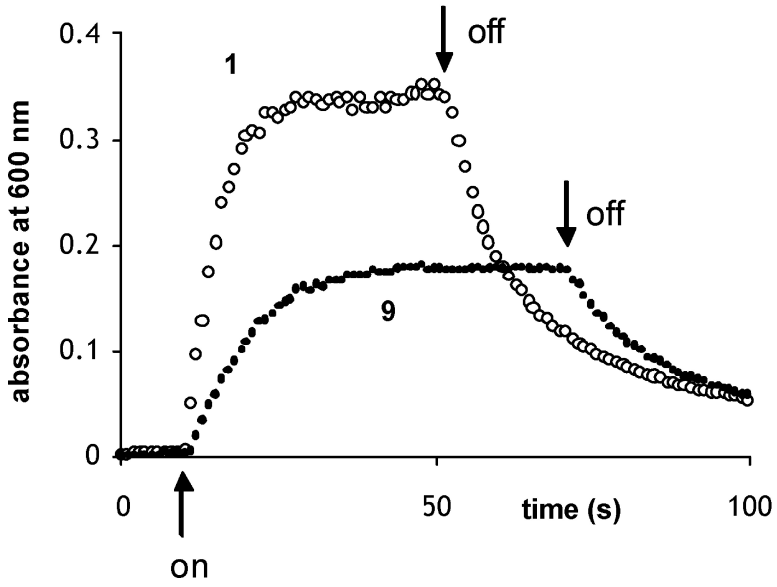

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Parallel Synthesis and Rapid Photochemical Screening of Organosoluble Ru^{II} Photosensitizers

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Ru^{II} complexes of heteroaromatic ligands are photosensitizers of interest in such applications as photovoltaic cells. Their bulk preparation is tedious, time-consuming, and expensive. Their assessments, by measurement of the individual excited-state lifetimes, is incomplete and requires specialized equipment and expertise, as well as time. The identification of new, promising photosensitizers would, therefore, greatly benefit from any time- and cost-saving protocol, if absolute purity is not required for assessment. This paper details a protocol for the fairly rapid preparation, in parallel and on a small scale, of organosoluble Ru^{II} complexes in a state ready for screening for photosensitization ability. The protocol was tested with a small set of bidentate ligands, generating 20 possible complexes, many of which are known. The protocol was found to produce predominantly the desired species in all cases except those with three different ligands. The batch screening results for the remaining 16 complexes were entirely consistent with those obtained with pure samples of the most promising materials prepared in bulk and were consistent with known photophysical properties.

Introduction

Ru^{II} complexes of heteroaromatic ligands are photoactive.[1] They can achieve photoinduced excited states with usefully long lifetimes by means of a metal-to-ligand charge transfer (MLCT) transition typically occurring in the blue region of the visible spectrum. The excited states can transfer energy or electrons to quenching molecules and, thus, sensitize these quenchers to the incident light. Such photosensitizers are of interest in such applications as photovoltaic cells, in which the excited states transfer an electron to an electrode, become oxidized in the process, and are reduced back to the starting state by a reductant, for instance, I^- from reduction of I_2, generated at the opposite electrode using the injected electron in the current produced between the electrodes. For optimal efficiency in this kind of application, new and better Ru^{II} complexes are needed.

The bulk preparation of Ru^{II} coordination complexes[2] uses an expensive Ru starting material and sometimes expensive ligands. It frequently requires high temperatures and long reaction times, owing to slow ligand exchange kinetics. The purification of the products, using chromatography, crystallization, or both, can be tedious and slow, and the overall yields of pure material are often only modest. The photosensitization ability can be assessed, albeit imperfectly, by measurement of the excited-state lifetime (τ), a measurement which requires time, care, anaerobic conditions, specialized equipment, and expertise. The identification of new Ru^{II} photosensitizers would therefore greatly benefit from any reduction in the required time and cost of preparation and assessment.

There have been comparatively few reports of combinatorial approaches to the identification of inorganic coordination complexes.[3] The Ru-containing targets have been mostly metathesis and polymerization catalysts[4] and, to our knowledge, do not include photoactive species. Yet, parallel synthesis can be well-suited for the identification of ligands and ligand combinations that confer useful properties to metal complexes. In the case of mononuclear, hexacoordinate Ru^{II} complexes binding n ligand moieties (six for unidentates, three for bidentates, or two for tridentates), the variety of combinations available from a set of N different ligands is $(N + n - 1)!/(N - 1)!n!$. Thus, a set of 13 tridentates or 7 bidentates could feasibly be tested simultaneously in a conventional 96-well setup. Combinations of tridentates with bidentates or unidentates in mono- or multinuclear assemblies could also be examined; however, combinations of ligands can produce mixtures of complexes. In the present case, two different bidentate ligands can form a mixture of four different Ru^{II} complexes, whereas three different ligands can lead to 10 different product complexes. The synthetic protocol must therefore promise a modicum of purity and yield for meaningful results.

Although it may be possible to expedite its measurement, the τ value is but one determinant of the photoactivity, others

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being the excited-state redox potentials, electron transfer rates, diffusion rates, and so on. We have recently described a photochemical means of assessing photosensitization ability.[5] In this method, the rate of appearance of the reduced form of a quencher is monitored spectroscopically while irradiating a sample in organic solvent containing the sensitizer, the quencher, and a sacrificial reductant to restore the Ru^{II} state. It is a comparative method in that new candidates are compared against previous benchmarks under identical conditions of irradiation, concentration, medium, and temperature. The method has the advantages of being reproducible and requiring no special care nor special equipment. We have applied the technique many times to assess individual sensitizers,[6] notably to explore electrostatic effects,[7] but because only a few seconds' worth of data suffices to assess a sample, the method can presumably serve as a screen for large numbers of samples. Another advantage is that it is a direct measure of the desired end result, photoproduct accumulation. It cannot address nor control the relative contributions of the underlying photophysical factors (τ, the extinction coefficient ϵ at the irradiating wavelength, electron-transfer rates, etc.), but unbiased, side-by-side comparisons enable the identification of better sensitizers whose photophysical attributes can later be examined in detail.

Before embarking on a search for better sensitizers in this way, we needed to be confident that a general, small-scale, synthetic protocol can, indeed, produce mixed-ligand products of the desired composition in sufficient purity and yield without having to isolate and confirm the identify of each product and to verify that the screen results will be consistent with the products' photophysical properties. We therefore chose to test the concept with a small set of known ligands, generating for these verifications a manageable number of combinations, most of which will be known compounds and several of which will have known photophysical properties. This paper details the implementation and testing of small-scale parallel synthesis and screening protocols for the fairly rapid identification of organosoluble Ru^{II} photosensitizers.

Experimental Section

General. Pure samples of $[Ru\mathbf{AC}_2]^{2+}$,[8] $[Ru\mathbf{A}_2\mathbf{B}]^{2+}$,[8] $[Ru\mathbf{BC}_2]^{2+}$,[9] $[Ru\mathbf{A}_2\mathbf{C}]^{2+}$,[8] $[Ru\mathbf{B}_2\mathbf{C}]^{2+}$,[9] and $[Ru\mathbf{C}_3]^{2+}$ [10] were prepared as their PF_6^- salts on a 0.1-g scale. The materials were from commercial sources and were used without further purification. $RuCl_3 \cdot 3H_2O$ and appropriate amounts of ligands **A**, **B**, and **C** were heated in ethane-1,2-diol at 140−160 °C, allowing 3 h for each of the first two ligand aliquots, then overnight for the third aliquot. Purification consisted of precipitation with aqueous NH_4PF_6 and chromatography on silica gel, using 28:2:1 CH_3CN-H_2O-saturated aqueous KNO_3 as eluent, followed by a second precipitation from CH_3CN solution using aqueous NH_4PF_6. The identities and purities of these materials were checked by TLC, ^1H NMR and UV−visible spectra in comparisons with literature data.[8−10] TLC analysis was performed on Macherey−Nagel silica gel plates using 28:2:1 CH_3CN-H_2O-saturated aqueous KNO_3 as developing solvent. ^1H NMR spectra were acquired in CD_3CN at 400 MHz on a Bruker ARX-400 machine.

Table 1. Sample Preparation Scheme: Sample Numbers for Samples Resulting from Mixing Ligands According to Column and Row Headings

	A + **A** +	**B** + **B** +	**C** + **C** +	**D** + **D** +	all except
A	1	2	3	4	5
B	6	7	8	9	10
C	11	12	13	14	15
D	16	17	18	19	20

Parallel Synthesis. Into each of 20 10-mL Pyrex tubes was placed 0.125 mL of 0.032 M $RuCl_3$ in CH_3OH, delivered via a Pipetman dispenser. A 0.125-mL aliquot of a 0.032 M solution in acetone or CH_3OH of ligand **A**, **B**, **C**, or **D**, according to the combinatorial scheme of Table 1, was added, followed by 0.5 mL of ethane-1,2-diol. The rack was placed in a silicone oil bath and heated for 3 h at 60 °C (bath temperature). The second ligand aliquot was then added, and heating was continued for another 3 h at 100 °C. After careful addition of the third aliquot, heating was continued at 170 °C overnight. After cooling to below 100 °C, excess aqueous NH_4PF_6 (0.8 M) was added. The tubes were centrifuged on a benchtop device for 30 min. The pale supernatant was drawn off with a disposable Pasteur pipet, and the dark pellet was resuspended in a few milliliters of fresh H_2O using a vortex mixer for a few seconds. The tubes were again centrifuged, and the supernatant was once more pipetted off. The tubes were then dried in a glassware oven at 80 °C overnight. TLC analysis was used to assess purity.

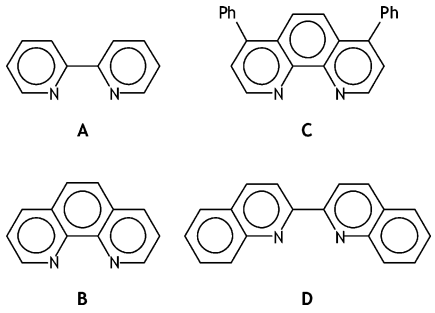
Photochemical Screening. Four milliliters of CH_3CN was added to each reaction tube with shaking to dissolve. From each, 0.1 mL of solution was transferred to a 3-mL disposable, polymethacrylate 1-cm-path length cuvette, to which was added 0.5 mL of a 0.05 M CH_3CN solution of $MV(PF_6)_2$, 0.5 mL of 0.25 M TEOA in CH_3CN, and 1.4 mL of fresh CH_3CN, to a final target concentration in Ru of 40 μM. The UV−visible spectrum was acquired, then the sample was irradiated, and its absorbance at 600 nm was monitored as described and using the same equipment as before.[5] Three irradiated growth and dark decay cycles were followed. The data were also treated as before to compute k_{init} values as the weighted average of least-squares values from each of the three growth cycles, with uncertainties computed as the weighted standard deviation of the values from the average, using the standard deviations in the least-squares fits as weights for both.

Results

Four readily available bidentate ligands (Chart 1) were chosen for testing of the combinatorial approach: 2,2′-bipyridine (**A**), 1,10-phenanthroline (**B**), 4,7-diphenyl-1,10-phenanthroline (**C**), and 2,2′-biquinoline (**D**), for a total of 20 different complexes containing all possible combinations of three ligands per metal. The fact that most of these complexes are known and that several have known τ values would enable a test of the protocols.

Parallel Synthesis and Screen. The combinatorial scheme employed is given in Table 1. Thus, sample 1 used 3 equiv of ligand **A**, sample 2 contained 2 equiv of **B** and one of **A**, sample 5 contained 1 equiv of all ligands but **A**, and so on. To ensure correct reaction stoichiometries at small scales,

Chart 1



the ligands and $RuCl_3$ were delivered as aliquots of stock solutions, each prepared in a convenient volatile solvent. The reaction mixtures were then diluted with a small volume of ethane-1,2-diol and heated, expelling the volatile solvents to leave a small reaction volume at high concentration. The reactions were conducted in small glass centrifuge tubes in the open, and the amount of Ru in each was 4 μmol, or <1 mg of $RuCl_3$. To maximize the production of the complexes whose compositions equal the reaction stoichiometries, the reactions were conducted in a stepwise manner, whereby the metal was allowed to react with each new equivalent of ligand at ever higher temperatures for increasing amounts of time, the reaction mixtures turning red in the process. In a further refinement of the procedure, the most basic and least hindered ligands (**A** > **B** > **C** > **D**) were added first, to minimize ligand scrambling during the last stage at the highest temperature. Workup consisted of adding aqueous NH_4PF_6 to each tube to precipitate the products as water-insoluble PF_6^- salts, centrifugation and decanting, resuspension of the pellet with fresh water to wash away residual solvent, a second centrifugation and decanting, then drying the rack of tubes in a glassware oven. The entire synthetic procedure required ~48 h.

For assessment of each sample, a portion of the dried crude product was transferred to a disposable cuvette, to which were added the electron acceptor methyl viologen (MV^{2+}) and the sacrificial reductant triethanolamine (TEA), to achieve the same final volume and reactant concentrations (maximal concentration in the case of the Ru complex) as had been used previously in the screening protocol.[5] The UV−visible spectrum was acquired to later compare the MLCT band positions with literature values, where available. In all cases, good matches with literature data were found.

Then, after equilibration to 25 °C, each sample was magnetically stirred and irradiated with blue light while monitoring the absorbance at 600 nm every 1 s, which indicates the presence of the reduced form of the acceptor ($MV^{\bullet+}$). In principle, 10 s of irradiation sufficed, the initial slope of the absorbance over time being the only numerical result needed. The slopes can be converted to pseudo-first-order rate constants k_{init} for the formation of $MV^{\bullet+}$ by dividing each by $\epsilon_{600}[MV^{2+}]_{init}$ (for a 1-cm cuvette), where ϵ_{600} is the extinction coefficient at 600 nm for $MV^{\bullet+}$. We have earlier shown that these k_{init} values are useful predictors of the true first-order rate constants k_f, which can only be computed by numerical modeling of the sigmoidal growth curve, and underestimate k_f by about 15%.

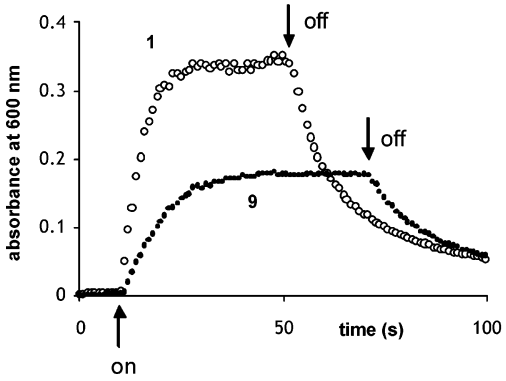


Figure 1. The first 100 s of two typical runs, showing the change in absorbance at 600 nm when the light source was turned on (up arrow) and off (down arrows) for samples 1 (open circles) and 9 (filled circles).

For testing and verification purposes, however, we continued to monitor the absorbance beyond this initial growth period. Figure 1 illustrates a typical run: the absorbance grows over ~20−50 s and reaches a steady state; it is sigmoidal because the concentration of $MV^{\bullet+}$ builds until its rate of quenching matches its photoinduced production. Turning the light off results in a second-order decay lasting some 300−400 s. A complete analysis of the photochemistry involved appeared earlier.[5] We took each sample through three growth-and-decay cycles to verify that each sample behaved normally, to check the reproducibility of the slope measurements, and to obtain statistically proper averages and uncertainties therein. In addition, the average absorbances A_{avg} over a 10-s period during steady state were computed for each cycle, as were uncertainties therein. This more complete assessment typically took less than 20 min per sample.

The left-over samples were examined by TLC, MS, and NMR in CD_3CN. The latter technique was found to be not particularly useful, because only the relatively uncomplicated signals from homoleptic complexes were readily detected in the single-ligand samples and as impurities in the mixed-ligand samples. Mass spectrometry (MALDI-TOF) was also complicated by fragmentation and by a poor correlation between relative concentration and relative signal strength. TLC was more useful: it revealed the presence of single major products in all cases except, not surprisingly, the four three-ligand samples (rightmost column of Table 1), which showed the presence of complex mixtures. We concluded that this synthetic protocol was not suitable for such complexes—indeed, special procedures have been developed for them[2,11]—and, although the screening *may* correctly pick out a three-ligand sample owing to a strong photoactivity from the corresponding three-ligand complex, such cannot be considered reliable.

Figure 2 provides the results for all 20 samples. In general, the A_{avg} correlated fairly well with k_{init} ($r = 0.90$), but because the steady-state absorbance level will depend on an uncontrolled O_2 concentration, k_{init} is a more reliable indicator of photosensitizer ability. Other authors have similarly used instantaneous or initial product accumulation rates.[12] Nevertheless, it was interesting that sample 6 disobeyed this correlation and had one of the largest A_{avg} values. According

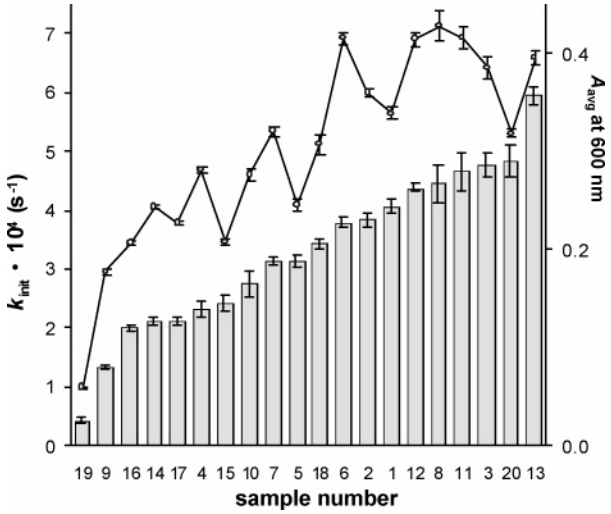


Figure 2. Values of k_{init} (columns, left scale) and A_{avg} (line, right scale), sorted by increasing k_{init} and with error bars indicating the experimental uncertainties.

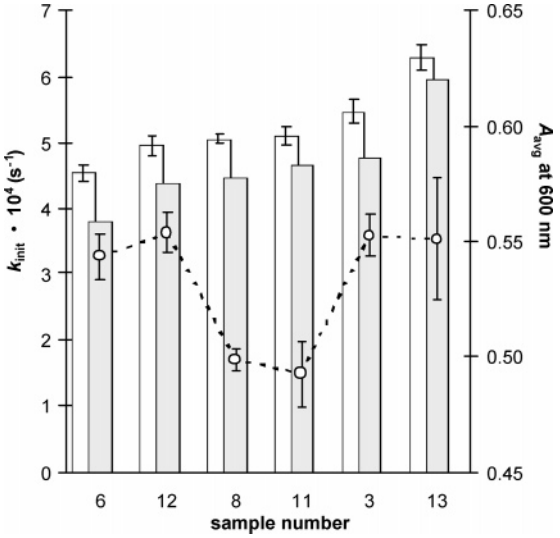


Figure 3. Values of k_{init} (white columns, left scale) and A_{avg} (dashed line, right scale) for the set of pure complexes, as compared to k_{init} values from crude preparations (hashed columns, left scale). The error bars indicate the experimental uncertainties.

to k_{init}, the best sensitizer was $[Ru\mathbf{C}_3]^{2+}$ (sample 13). The difference between its activity and that of the next best was statistically very significant, whereas the next five best were pairwise statistically indistinguishable, and their ordering was not precisely determinable. On average, complexes containing **C** did best, those with **A** fared a little better than those with **B**, and those with **D** populated the low end of the activity range. The performance of the **D**-containing species may be biased by steric hindrance, which would decrease yields and purity, rather than any innate deficiency. The activities of the three-ligand samples, which we discounted on the basis of being unreliably complex, were unremarkable, except for the **D**-free sample (number 20), the activity of which may be due to a favorable mix of homoleptic and heteroleptic species, rather than necessarily to $[Ru\mathbf{ABC}]^{2+}$ itself (vide infra).

Screen of Pure Sensitizers. To confirm the results and ensure that they were representative, we separately prepared pure bulk samples of each of the five most active single- and two-ligand complexes (samples 3, 8, 11, 12, and 13) and added sample 6, since it showed one of the highest A_{avg} values. This generous sampling (33%) was meant to catch possible cases in which yield or purity issues could have been depressing the detected photoactivities. The bulk preparations used conventional but unoptimized methods, including purification by chromatography and crystallization. After verifying the product identities as, indeed, corresponding to the reaction stoichiometries by NMR and against literature UV−visible data, we submitted each of these six to the same photochemical screen under identical conditions. This time, however, the sensitizer concentrations were known. Gratifyingly, we found that the pure samples at fixed concentrations had somewhat higher activities than their unpurified, small-scale counterparts, for which the concentrations were lowered by the isolation steps and were limited by product purity. The relative sensitizer utilities according to k_{init} (Figure 3) were also the same, with $[Ru\mathbf{C}_3]^{2+}$ the confirmed best. Samples 8, 11, and 12 were statistically indistinguishable but formed a third-place group that was statistically significantly different from the other samples. In these runs, A_{avg} values proved to be much less useful, with four of the six values being statistically indistinguishable, and less well related to the k_{init} values. Further, these A_{avg} values were very poorly correlated to the values from the crude preparations ($r = -0.66$), whereas the k_{init} values were very strongly correlated to the earlier values ($r = 0.99$). These findings demonstrate the superior reliability of the k_{init} values. Sample 6, $[Ru\mathbf{A}_2\mathbf{B}]^{2+}$, which had been included in this group because of a very high A_{avg} value in the crude state, was decidedly deemed a sensitizer of comparatively modest utility.

$$Ru^{II} \overset{k_1}{\rightleftharpoons} Ru^{II}* \quad (1)$$

$$Ru^{II}* + MV^{2+} \xrightarrow{k_{init}} Ru^{III} + MV^{\bullet+} \quad (2)$$

Relation to Photophysical Properties. Using the abbreviated kinetic picture related by eqs 1 and 2,[5] we reason that k_{init} will be proportional to the excited-state concentration $[Ru^{II}*]$, which in turn will be given by $k_1[Ru^{II}]_0/k_{-1}$. Among other factors, k_1 will depend on ϵ_{max}, relating the ability of a sensitizer to become excited, whereas k_{-1} is $1/\tau$, which relates the ability of a sensitizer to stay excited long enough to undergo a collision with MV^{2+}. We therefore expect k_{init} to be proportional to $\epsilon_{max}\tau$. All of the complexes that we rescreened in the pure state are known, and room-temperature excited-state lifetimes (τ) are available for all. Unfortunately, the lifetimes have been measured by different groups under different conditions and are not altogether consistent. Data for $[Ru\mathbf{B}_2\mathbf{C}]^{2+}$ (2560 ns) and $[Ru\mathbf{C}_3]^{2+}$ (5340 ns) were obtained in MeOH.[13] Values for $[Ru\mathbf{A}_2\mathbf{C}]^{2+}$ (1970 ns) and $[Ru\mathbf{AC}_2]^{2+}$ (4100 ns), obtained in EtOH,[14] were corrected to MeOH by scaling against the lifetimes of $[Ru\mathbf{C}_3]^{2+}$ in EtOH (4890 ns)[14] and MeOH.[13] Similarly, the value for $[Ru\mathbf{A}_2\mathbf{B}]^{2+}$ in CH_2Cl_2 (310 ns)[15] was scaled using the lifetimes of $[Ru\mathbf{A}_3]^{2+}$ in CH_2Cl_2 (490 ns)[15] and MeOH (765 ns).[16] Somewhat shorter lifetimes were reported in aqueous solution[8] but they did not follow the same order. Since CH_2-

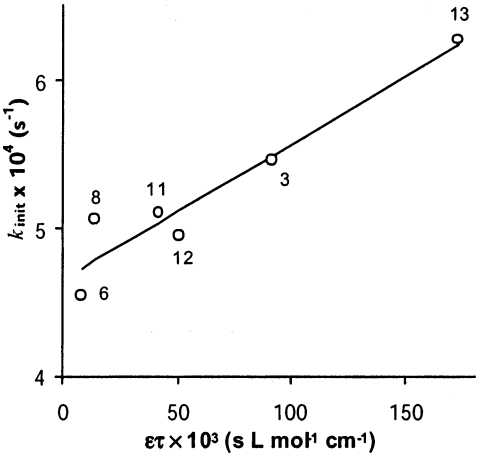


Figure 4. Plot of k_{init} (open circles) vs $\epsilon\tau$ and the least-squares fit (line). Sample numbers appear next to each point.

Cl_2 more closely resembles the solvent used here than does H_2O, we used the CH_2Cl_2 data. For $[Ru\mathbf{BC}_2]^{2+}$, only the value for the ClO_4^- salt in aerated H_2O (770 ns) was available,[17] and this was similarly corrected using the lifetimes of $[Ru\mathbf{B}_3]^{2+}$ in this medium (459 ns)[17] and in MeOH (313 ns).[16] Using these MeOH-harmonized τ values and the ϵ values that we measured just before the photochemistry runs, we found that k_{init} indeed correlated very well ($r = 0.96$) with $\epsilon\tau$ (Figure 4) for the six sensitizers examined in the pure state at fixed concentrations. Virtually the same level of correlation was found when the τ values were corrected to EtOH, instead, or when the integrated absorbance over the entire 400−600-nm region was used instead of ϵ at λ_{max}. From a statistical point of view, correlations such as this between error-prone sets of data are to be interpreted with caution, especially so in the present case, in which the τ values are uncertain. Nevertheless, $[Ru\mathbf{C}_3]^{2+}$, with the largest ϵ and τ values, showed the greatest activity, whereas $[Ru\mathbf{A}_2\mathbf{B}]^{2+}$, which has the smallest ϵ and τ values, showed the weakest activity of the six. We consider this correlation a satisfactory demonstration of the utility of the k_{init} measurements in identifying the best sensitizers.

Finally, the poor photoactivity of **D**-containing samples can be understood in photophysical terms. Data are not available for many, but $[Ru\mathbf{D}_3]^{2+}$ is reported to be only very weakly emissive at room temperature, whereas $[Ru\mathbf{AD}_2]^{2+}$ and $[Ru\mathbf{A}_2\mathbf{D}]^{2+}$ have significantly shorter lifetimes than $[Ru\mathbf{A}_3]^{2+}$.[18] According to low-temperature or variable-temperature τ measurements,[19−21] which do not always agree, **D**-containing complexes appear to have generally lower τ values than do **A**- or **B**-containing analogues (for instance, 2.9 μs for $[Ru\mathbf{D}_3]^{2+}$ vs 5.3 μs for $[Ru\mathbf{A}_3]^{2+}$ and 9.8 μs for $[Ru\mathbf{B}_3]^{2+}$ in 4:1 EtOH/MeOH at 77 K).[21] In the case of $[Ru\mathbf{D}_3]^{2+}$, steric congestion leads to longer Ru−N bonds, a reduced ligand field, and a relatively low-lying, nonemissive but rapidly decaying ^{3}MC state.[20] It also leads to chemical instability[21] and a susceptibility to photodissociate.[20] Steric hindrance will be less severe in the mixed-ligand complexes, but we expect that the composition of the crude samples will have been steered away from the **D**-containing species.

Discussion

Only a portion of each synthetic sample was used in the screening step. This allowed us to perform analyses on the remainders, but the sample sizes might be reduced further in routine applications. We did not explore smaller reaction scales; at some lower limit, the precipitation and centrifugation steps might not have visible effects. The scale of our protocol was instead chosen to avoid volume errors in the dilution of the crude sample pellet and in the transfer of an aliquot of the resulting solution. All in all, only 17 mg of $RuCl_3$ was used, and virtually all of the metal is recoverable, including material that fails to precipitate or that might redissolve in the H_2O rinse, as the supernatants can be directed to a Ru waste stream.

Our allocation of time for each ligand attachment step was generous—the protocol is meant to work with recalcitrant reactants—and demonstrates that no untoward harm is occasioned by prolonged reaction times. Without having explored minimum times needed, they can doubtless be reduced somewhat without much affecting the final results. As with the screening step, the synthetic protocol used unspecialized equipment commonly available in any preparative laboratory. The individual reaction steps could doubtless be shortened with microwave irradiation, but the total time requirement for many samples can be significantly reduced to any extent by this means only if several samples can be irradiated at once, using specialized ovens, whereas it is simple to heat many samples in a large oil bath.

The screening protocol described herein relies on a high enough reaction yield and sufficient product solubility to deliver an adequate amount of a product from a given reaction stoichiometry for the measured relative photoactivity to accurately reflect the innate activity of the pure substance of corresponding composition. The stepwise addition of ligands, the prolonged reaction times, and the generous reaction temperatures helped to maximize the yields and purities of desired product salts. The last ligand attachment step is the slowest but produces an ionic product. The anion exchange/precipitation step with NH_4PF_6 not only adds a significant amount of mass to the small samples produced, but also serves to reduce the presence of any neutral products of incomplete reactions ($LRuCl_3$ and $LL'RuCl_2$). The PF_6^- anions also confer organosolubility, which is required in the screening step because the photochemical assessment method fails in aqueous solutions. Clearly, incomplete reactions with low yields and products of low organosolubility will reduce the amount of photoactive species in the cuvette samples. In this way, the photochemical screen also discriminates on the basis of yield and solubility. These factors, together with the availability and cost of ligands, contribute to the overall photosensitizer availability and, along with photoactivity, are encompassed in a broad but pragmatic definition of photosensitizer *utility*. In any case, it would have been tedious and difficult to have done otherwise. The photochemical results could feasibly be numerically deconvoluted so as to uncover the innate activities of pure compounds, even in complex mixtures, provided that the concentration of each component was available for each sample. This would require weighing the sample pellets, which is highly error-prone at

the small scale used, and a determination of the sample compositions, by HPLC or other means, which requires a considerable amount of time and expense and specialized instruments. By numerical simulation of the sample activities from various sample composition scenarios, one can convince oneself that the screening step will correctly point to the most photoactive species, so long as the desired species, that whose composition corresponds to the reaction stoichiometry, is dominant. To accommodate error, however, the screen should be used to pick several candidates for further examination in the pure state instead of being relied upon to pick only the very best candidate.

Conclusion

We have demonstrated the benefits of a small-scale parallel synthetic protocol combined with a photochemical screen to correctly identify organosoluble Ru^{II} photosensitizers of high photochemical activity from crude reaction mixtures in which other photoactive complexes can occur as side-products. From the limited set of ligands examined, we conclude that $[Ru\mathbf{C}_3](PF_6)_2$ is the most *useful* sensitizer in CH_3CN at room temperature, where the notion of *utility* includes *availability* as well as photoactivity, and this finding is supported by photophysical data. The process uses little material, and the metal is recoverable; it requires no special equipment or special sample handling, and much less time and material than do conventional single-sample techniques. The protocol can confidently be extended to larger numbers of ligand combinations, as well as to select for other properties, for instance, luminescence intensity, oxidation potential, DNA binding ability, etc.

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