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Effective utilization of NIR wavelengths for photo-controlled polymerization – penetration through thick barriers and parallel solar syntheses

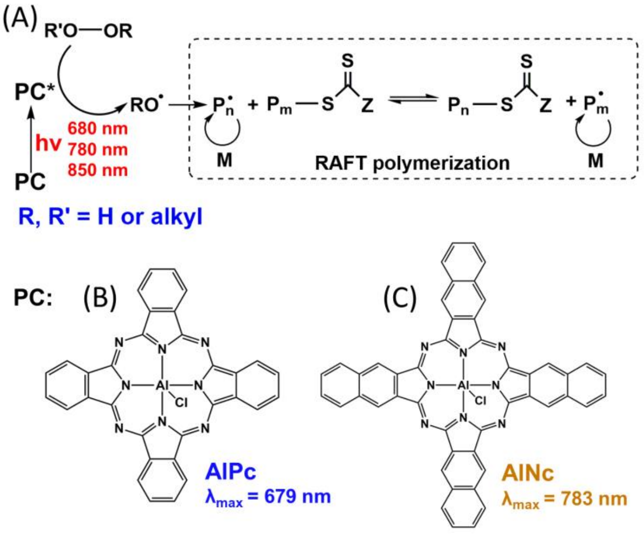
Zilong Wu,[a] Kenward Jung,*[a] and Cyrille Boyer*[a]

Abstract: This contribution details an efficient and controlled photopolymerization regulated by far-red (λ = 680 nm) and NIR (λ = 780 and 850 nm) light in the presence of aluminum phthalocyanine and aluminum naphthalocyanine. Initiating radicals are generated by photosensitization of peroxides affording an effective strategy that provides controlled polymerizations of a variety of monomers with excellent living characteristics. Critically, the long wavelength irradiation provides penetration through thick barriers, affording unprecedented rates of controlled polymerization that can open new and exciting applications. Furthermore, a more optimized approach to performing solar syntheses is presented. By combining the narrow Q-bands of these PCs with others possessing complementary absorptions, layered, independent polymerizations and organic transformations may be performed in parallel under a single broadband emission source such as sunlight.

Since Ciamician's visionary address over a century ago,[1] photochemistry continues to evolve to fuel innovation across broad research areas. Alongside the intense focus on utilizing the Sun as a renewable energy source,[2] light-mediated chemical syntheses have also received significant attention through the years.[3] In particular, the advent of photoredox catalysis has spurred the utilization of lower energy visible wavelengths, overcoming the non-specificity of high energy ultraviolet irradiation.[4]

Echoing these developments, a wide range of controlled photopolymerizations regulated by visible wavelengths have been developed,[5] creating new opportunities in the preparation of functional materials.[6] Although visible and UV light mediated polymerizations are now well established,[7] there have been very few examples utilizing far-red or near infra-red (NIR) light due to their lower energy.[8] The enhanced penetration of non-transparent materials by these wavelengths are promising for the development of new and exciting applications.[9] Moreover, with more than 50% of the solar spectrum constituted of longer wavelengths beyond the visible spectrum,[10] expanding our photochemical capabilities to far-red and NIR wavelengths provides a gateway to more optimized usage of sunlight for photochemical syntheses.[11]

Herein, we report a photoinitiation system regulated by far-red to NIR light utilizing the strong Q-bands of aluminum phthalocyanine (AlPc; λ_{max} = 679 nm), and aluminum napthalocyanine (AlNc; λ_{max} = 783 nm) (**Figure S1**, **Table S1**). Previous investigations examining phthalocyanines for photodynamic therapy have revealed their capacity to photosensitize (hydro)peroxides to form radical species under long wavelength irradiation (**Scheme 1**);[12] a capability that has yet to be exploited for photochemical syntheses. We reasoned that combining this initiation pathway with reversible addition fragmentation chain transfer (RAFT) polymerization would yield an effective controlled polymerization process regulated by longer wavelengths. The surprising efficiency of this process affords unprecedented rates of controlled polymerization in the order of minutes even through barriers. Moreover, the narrow absorptions of the model AlPc and AlNc compounds provide a novel approach to utilizing sunlight for chemical syntheses; in combination with PCs possessing complementary absorptions in the visible spectrum, we demonstrate the ability to perform multiple independent photochemical reactions in parallel under a single broadband emission source.



Scheme 1. (**A**) Long wavelength photosensitization of (hydro)peroxides to generate radicals under far-red and NIR wavelengths mediated by (**B**) aluminum phthalocyanine (AlPc) and (**C**) aluminum naphthalocyanine (AlNc).

A variety of peroxides were first screened (**Table S2**); among the peroxides that only proceeded when irradiated in the presence of the photocatalysts (PCs), urea hydrogen peroxide (UHP) provided the fastest rates and was selected for in depth study. In contrast, the non-stabilized hydrogen peroxide promoted polymerization in the absence of catalyst or irradiation. The photoinitiation system displayed excellent temporal control, which was demonstrated by the absence of monomer conversion in the dark (**Figure 1A**, **D**), even for off periods as long as 24 hours

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(**Figure S3D**); resuming the light exposure reactivated the polymerization with little to no changes to the propagation rate (**Figure S2**, **Figure S3A-C**, **Table S2**).[13] Interruptions to the irradiation had no effect on the controlled behaviour as confirmed by the linear evolution of M_n with increasing monomer conversion (**Figure 1B**, **E**). Save for some low molecular weight tailing and high molecular weight shoulders arising from termination reactions, the molecular weight distributions (MWDs) were mostly narrow and symmetrical, with clear shifts towards higher molecular weight occurring under light exposure only (**Figure 1C**, **F**, **Figure S3D**).

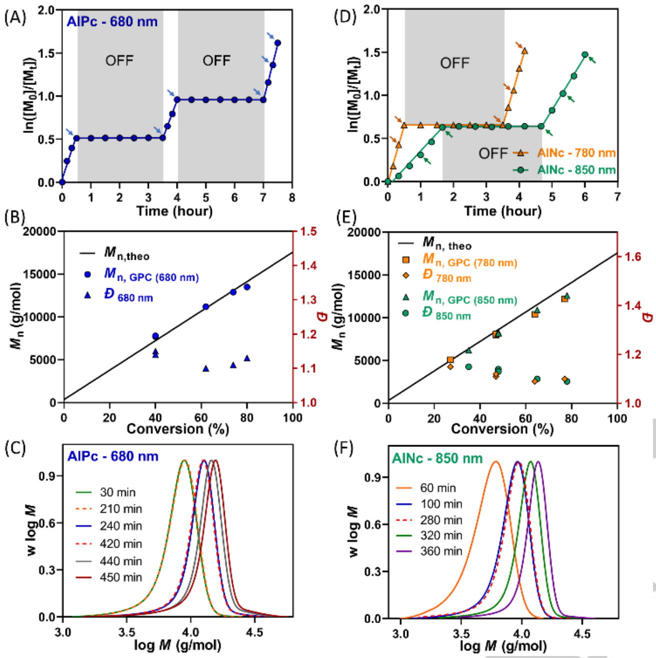

Figure 1. Demonstration of temporal control for AlPc and AlNc mediated RAFT photopolymerization of methyl acrylate under 680 nm (I = 4 mW cm^{-2}), 780 nm (I = 20 mW cm^{-2}) and 850 nm (I = 55 mW cm^{-2}) irradiation with a reaction composition consisting of [MA]:[DTPA]:[UHP]:[PC] = 200 : 1 : 0.2 : 0.002 in DMSO. (**A**) and (**D**) ln([M]$_0$/[M]$_t$) versus exposure time according to the designated ON (white) / OFF (gray) profile; (**B**) and (**E**) evolution of M_n and Đ versus monomer conversion and (**C**) and (**F**) evolution of the MWDs generated in the ON/OFF experiments.

Monomer compatibility was verified by polymerizing methyl acrylate (MA), methyl methacrylate, *N*-isopropylacrylamide and *N*-isopropylmethacrylamide as model monomers (**Table S3**; **Figure S4**) and were observed to proceed as expected with good control demonstrated under all three wavelengths. Chain extensions also proceeded in a predictable manner with a clean shift of MWD towards higher molecular weight (**Figure S5D-I**). Excellent chain end fidelity as confirmed via a combination of ^{1}H NMR analyses (**Figure S6**, **Table S4**) and close match of the RI and UV gel permeation chromatography (GPC) chromatograms (**Figure S5A-C**), permitted higher degrees of polymerization (DP) ranging from 50 to 5,000, which resulted in relatively narrow and symmetric MWDs ($Đ$ < 1.5) (**Figure S7**, **Table S5**). The effect of the PC concentration was examined under the three wavelengths by comparative kinetic studies of MA using a fixed light intensity of 20 mW cm^{-2} (**Figure 2A**, **Figure S8A-C**). Increasing PC concentrations from 10 to 50 ppm resulted in a concomitant increase in the observed propagation rate coefficient (k_p^{app}); the modest increases observed for AlNc under 850 nm light was attributed to its significantly lower extinction coefficient at this wavelength. More significant effects were noted from increasing the light intensity; at a fixed PC concentration of 50 ppm, increasing the light intensity from 20 to 40 mW cm^{-2} resulted in a substantial increase in k_p^{app} (0.16 min^{-1}) for AlPc (λ = 680 nm), leading to high monomer conversion (> 70%) in about 10 minutes (**Figure 2B**, **Figure S8D**). Further increasing the light intensity to 100 mW cm^{-2} afforded the same k_p^{app} (0.16 min^{-1}) for AlNc under 780 nm light with the k_p^{app} increasing to ~ 0.07 min^{-1} under 850 nm light (**Figure 2B**, **Figure S8E**, **F**), leading to similarly high conversion (> 70%) in about 15 and 30 minutes, respectively.

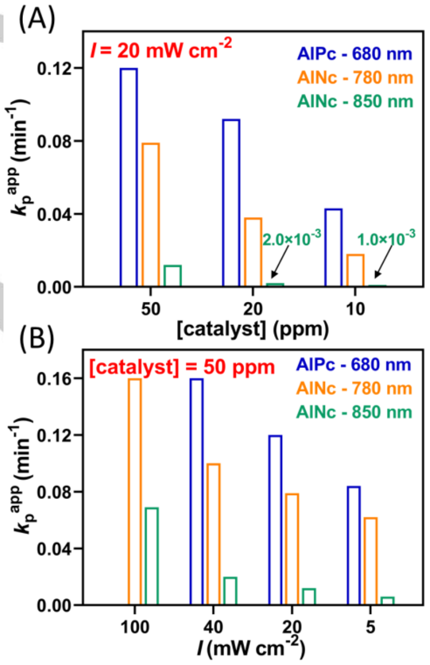

Figure 2. (**A**) Evolution of apparent propagation rates (k_p^{app}) of MA polymerizations with increasing AlPc and AlNc concentrations under 680, 780 and 850 nm light at a fixed intensity of 20 mW cm^{-2}. (**B**) Evolution of k_p^{app} 's of MA photopolymerizations with increasing light intensity (5-100 mW cm^{-2}) using fixed AlPc and AlNc concentrations under 680, 780 and 850 nm light.

The fast polymerization rates indicated unprecedented capability to polymerize behind barriers in comparison to previous studies.[8d, 8j, 8o, 14] Photopolymerizations performed through paper (thickness ~ 0.10 and 0.2 mm) proved to be successful under all three wavelengths (**Figure 3A**, **Figure S9D-F**). Despite significant reductions to the light intensity (**Table S6**), high monomer conversions (> 80 %) were achieved in about 25 and 40 mins for AlPc (680 nm) and AlNc (780 nm), respectively (**Table S7**). Polymerizations performed through chicken skin (1 mm), mediated by AlNc under NIR wavelengths incurred less penalties to the k_p^{app} in comparison to paper, hinting at the superiority of these wavelengths through biological barriers (**Figure 3A**, **Figure**

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S9D-**F**). Surprisingly, AlPc mediated polymerizations under 680 nm light proceeded through pig skin with relatively fast rates even through thicknesses as high as 5 mm and afforded high conversions (> 80%) in less than 30 minutes of exposure time. Increasing the thickness to 15 mm saw the polymerization rates plummet for all three wavelengths as expected. Interestingly, the limited absorption of 850 nm light by AlNc was offset by its superior penetration through the 15 mm thick barrier (**Table S6**) and enabled the fastest rates of polymerizations among the studied PCs. The advantage of NIR wavelengths were epitomized by polymerizations performed through an opaque blue polypropylene barrier (2.5 mm) wherein only the NIR wavelengths (λ_{em} = 780 nm and 850 nm) were able to generate polymers (**Table S7** #19-21). Critically, fast kinetics, that appeared to be relatively unimpeded by the barrier, were achieved using 850 nm light with a k_p^{app} ($k_p^{app}{}_{PP}$ = 0.053 min^{-1} vs $k_p^{app}{}_{direct}$ = 0.069 min^{-1}) (**Figure S10**). These results showcase the high efficiency of the PCs in utilizing longer wavelengths to facilitate controlled photopolymerizations even through thick barriers.

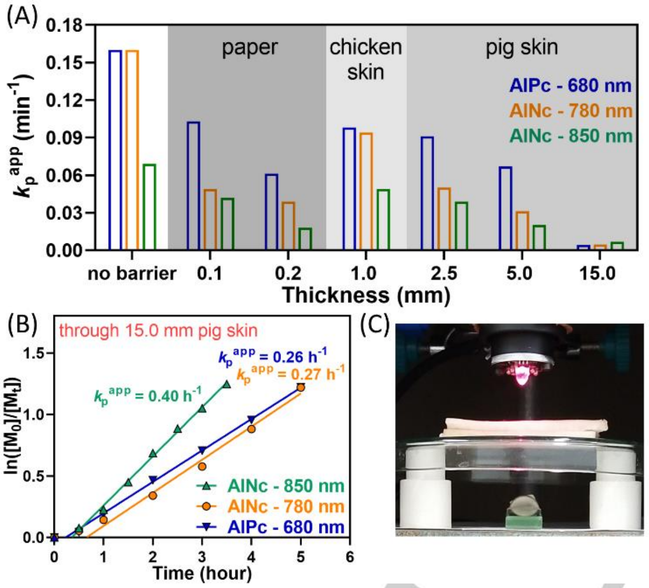

Figure 3. RAFT photopolymerizations of MA mediated by AlPc and AlNc under far-red (λ_{max} = 680 nm; I = 40 mW cm^{-2}) and NIR (λ_{max} = 780 nm; I = 100 mW cm^{-2} and λ_{max} = 850 nm; I = 100 mW cm^{-2}) light through barriers. (**A**) Comparison of apparent propagation rate coefficients (k_p^{app}). (**B**) Kinetic comparison of RAFT photopolymerizations performed through 15.0 mm thick pig skin. (**C**) Photo detailing the experimental setup used for polymerizing through 5.0 mm pig skin.

Having confirmed the high efficiency of this process under low energy wavelengths, we considered the application of this current system for sunlight driven synthesis. The incorporation of complementary dyes to maximize light harvesting has become an established strategy in the development of dye-sensitized solar cells; however, such a concept has not been applied to photochemical syntheses.[15] We envisioned the use of a similar strategy to perform chemical syntheses under broadband emissions with one key difference; PCs with narrow but complementary absorptions may be superposed in segregated reaction vessels, allowing unused photons to pass through to the lower layers, enabling independent reactions to be performed in a simultaneous manner (**Figure 4A**, **Scheme S3**). To demonstrate this concept, we employed *fac*-[Ir(ppy)$_3$], eosin Y (EY), AlPc and AlNc as PCs with complementary absorptions to optimize the usage of broadband solar emission (AM 1.5G, 1000 W m^{-2}) (**Figure 4B**).

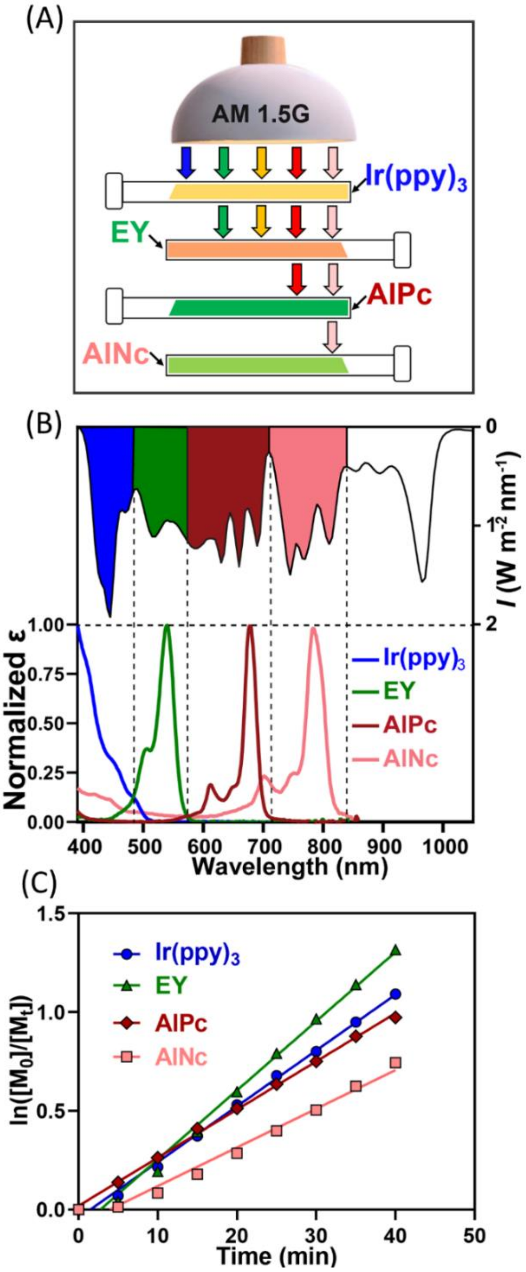

Figure 4. (**A**) Schematic of layered independent reactions ordered by (top to bottom) *fac*-Ir(ppy)$_3$ (λ_{max} = 390 nm), eosin Y (EY; λ_{max} = 540 nm), AlPc (λ_{max} = 678 nm) and AlNc (λ_{max} = 783 nm) irradiated by simulated sunlight (AM 1.5G). (**B**) Comparison of simulated AM 1.5G emission (top) and the normalized absorption spectra of layered PCs. (**C**) Kinetic comparison of photopolymerizations mediated by the layered PCs.

The principle of segregating the PCs affords the opportunity to perform independent chemical syntheses using a single emission source; four independent polymerization reactions were stacked in the order of: (1) an Ir(ppy)$_3$ mediated PET-RAFT polymerization,[16] (2) an EY and triethylamine (TEA) mediated PET-RAFT polymerization,[17] (3) AlPc and (4) AlNc mediated photopolymerizations using red and NIR light respectively (**Figure 4C**, **Table S8**, **Figure S11**). These photopolymerizations, mediated by different segments of the simulated solar emission proceeded in a controlled manner in accord with our previous results. This layered or stacked approach is also compatible with organic transformations as demonstrated by the successful implementation of 2 organic (atom transfer radical addition[18] and thiol-ene[19]) and 2 polymerization reactions performed simultaneously in segregated reaction vessels (**Table S9**, **Figure S12**).

This contribution details a fast and highly efficient controlled photopolymerization process regulated by far-red and NIR wavelengths by exploiting the Q-bands of model metallophthalocyanines. The enhanced penetration capabilities afforded by the low energy wavelengths, in conjunction with the efficiency of this process, promoted unprecedented polymerization rates (order of minutes) through synthetic and biological (chicken and pig skin) barriers. The complementary absorption characteristics of these PCs to existing catalysts enables the layered superposition of multiple independent and simultaneous reactions, providing a model for more optimized usage of broadband solar emission that can also facilitate miniaturization of photochemical reactors. Furthermore, the variety of modifications available for further red-shifting the Q-band of these PCs[20] is promising for the utilization of even longer wavelengths in the NIR region and beyond.

Keywords: Photopolymerization • NIR • Solar synthesis • Reversible-deactivation radical polymerization • Photochemistry

[1] G. Ciamician, *Science* **1912**, *36*, 385-394.

[2] a) N. S. Lewis, *Science* **2007**, *315*, 798-801; b) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050-6051.

[3] a) H. D. Roth, *Angew. Chem. Int. Ed.* **1989**, *28*, 1193-1207; b) V. Balzani, G. Bergamini, P. Ceroni, *Angew. Chem. Int. Ed.* **2015**, *54*, 11320-11337; c) D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Rev.* **2016**, *116*, 10276-10341; d) K. Glusac, *Nat. Chem.* **2016**, *8*, 734.

[4] a) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102-113; b) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828-6838; c) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322-5363.

[5] a) S. Chatani, C. J. Kloxin, C. N. Bowman, *Polym. Chem.* **2014**, *5*, 2187-2201; b) M. Chen, M. Zhong, J. A. Johnson, *Chem. Rev.* **2016**, *116*, 10167-10211.

[6] a) R. Langer, D. A. Tirrell, *Nature* **2004**, *428*, 487-492; b) J. Niu, D. J. Lunn, A. Pusuluri, J. I. Yoo, M. A. O'Malley, S. Mitragotri, H. T. Soh, C. J. Hawker, *Nat. Chem.* **2017**, *9*, 537; c) B. S. Tucker, M. L. Coughlin, C. A. Figg, B. S. Sumerlin, *ACS Macro Lett.* **2017**, *6*, 452-457; d) T. Lueckerath, T. Strauch, K. Koynov, C. Barner-Kowollik, D. Y. W. Ng, T. Weil, *Biomacromolecules* **2019**, *20*, 212-221.

[7] a) B. P. Fors, C. J. Hawker, *Angew. Chem. Int. Ed.* **2012**, *51*, 8850-8853; b) D. Konkolewicz, K. Schröder, J. Buback, S. Bernhard, K. Matyjaszewski, *ACS Macro Lett.* **2012**, *1*, 1219-1223; c) X. Pan, M. Lamson, J. Yan, K. Matyjaszewski, *ACS Macro Lett.* **2015**, *4*, 192-196; d) X. Pan, C. Fang, M. Fantin, N. Malhotra, W. Y. So, L. A. Peteanu, A. A. Isse, A. Gennaro, P. Liu, K. Matyjaszewski, *J. Am. Chem. Soc.* **2016**, *138*, 2411-2425; e) L. Shen, Q. Lu, A. Zhu, X. Lv, Z. An, *ACS Macro Lett.* **2017**, *6*, 625-631.

[8] a) B. Strehmel, C. Schmitz, K. Cremanns, J. Göttert, *Chemistry – A European Journal*, *0*; b) Y. Yagci, S. Jockusch, N. J. Turro, *Macromolecules* **2010**, *43*, 6245-6260; c) E. H. Discekici, A. Anastasaki, J. Read de Alaniz, C. J. Hawker, *Macromolecules* **2018**, *51*, 7421-7434; d) S. Shanmugam, J. Xu, C. Boyer, *Angew. Chem. Int. Ed.* **2016**, *55*, 1036-1040; e) N. Corrigan, J. Xu, C. Boyer, *Macromolecules* **2016**, *49*, 3274-3285; f) C. Ding, J. Wang, W. Zhang, X. Pan, Z. Zhang, W. Zhang, J. Zhu, X. Zhu, *Polym. Chem.* **2016**, *7*, 7370-7374; g) M. K. Darani, S. Bastani, M. Ghahari, P. Kardar, E. Mohajerani, *Prog.n Org. Coat.* **2017**, *104*, 97-103; h) A. H. Bonardi, F. Dumur, T. M. Grant, G. Noirbent, D. Gigmes, B. H. Lessard, J. P. Fouassier, J. Lalevée, *Macromolecules* **2018**, *51*, 1314-1324; i) C. Kütahya, C. Schmitz, V. Strehmel, Y. Yagci, B. Strehmel, *Angew. Chem. Int. Ed.* **2018**, *57*, 7898-7902; j) H. Cao, G. Wang, Y. Xue, G. Yang, J. Tian, F. Liu, W. Zhang, *ACS Macro Lett.* **2019**, *8*, 616-622; k) K. K. Childress, K. Kim, D. J. Glugla, C. B. Musgrave, C. N. Bowman, J. W. Stansbury, *Macromolecules* **2019**, *52*, 4968-4978; l) C. Schmitz, Y. Pang, A. Gülz, M. Gläser, J. Horst, M. Jäger, B. Strehmel, *Angew. Chem. Int. Ed.* **2019**, *58*, 4400-4404; m) Z. Li, X. Zou, F. Shi, R. Liu, Y. Yagci, *Nat. Commun.* **2019**, *10*, 3560; n) Z. Li, J. Zhu, X. Guan, R. Liu, Y. Yagci, *Macromolecular Rapid Communications* **2019**, *40*, 1900047; o) B. D. Ravetz, A. B. Pun, E. M. Churchill, D. N. Congreve, T. Rovis, L. M. Campos, *Nature* **2019**, *565*, 343-346.

[9] J. Elisseeff, K. Anseth, D. Sims, W. McIntosh, M. Randolph, R. Langer, *Proc. Nat. Aca. Sci. USA* **1999**, *96*, 3104-3107.

[10] M. P. Thekaekara, *Solar Energy* **1976**, *18*, 309-325.

[11] a) P. Esser, B. Pohlmann, H.-D. Scharf, *Angew. Chem. Int. Ed.* **1994**, *33*, 2009-2023; b) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527; c) D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176; dM. Oelgemöller, *Chem. Rev.* **2016**, *116*, 9664-9682.

[12] a) T. G. Gantchev, W. M. Sharman, J. E. Van Lier, *Photochem. Photobio.* **2003**, *77*, 469-479; b) T. G. Gantchev, J. E. van Lier, *Chem. Phys. Lett.* **2003**, *369*, 627-634.

[13] N. D. Dolinski, Z. A. Page, E. H. Discekici, D. Meis, I.-H. Lee, G. R. Jones, R. Whitfield, X. Pan, B. G. McCarthy, S. Shanmugam, V. Kottisch, B. P. Fors, C. Boyer, G. M. Miyake, K. Matyjaszewski, D. M. Haddleton, J. R. de Alaniz, A. Anastasaki, C. J. Hawker, *J. Polym. Sci. Part A: Polym. Chem.* **2019**, *57*, 268-273.

[14] J. Jiang, G. Ye, F. Lorandi, Z. Liu, Y. Liu, T. Hu, J. Chen, Y. Lu, K. Matyjaszewski, *Angew. Chem. Int. Ed.* **2019**, *58*, 12096-12101.

[15] aN. Robertson, *Angew. Chem. Int. Ed.* **2006**, *45*, 2338-2345; bB. E. Hardin, H. J. Snaith, M. D. McGehee, *Nat. Photo.* **2012**, *6*, 162.

[16] J. Xu, K. Jung, A. Atme, S. Shanmugam, C. Boyer, *J. Am. Chem. Soc.* **2014**, *136*, 5508-5519.

[17] a) I.-H. Lee, E. H. Discekici, A. Anastasaki, J. R. de Alaniz, C. J. Hawker, *Polym. Chem.* **2017**, *8*, 3351-3356; b) C. A. Figg, J. D. Hickman, G. M. Scheutz, S. Shanmugam, R. N. Carmean, B. S. Tucker, C. Boyer, B. S. Sumerlin, *Macromolecules* **2018**, *51*, 1370-1376.

[18] C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2012**, *134*, 8875-8884.

[19] aC. E. Hoyle, C. N. Bowman, *Angew. Chem. Int. Ed.* **2010**, *49*, 1540-1573; bM. J. Kade, D. J. Burke, C. J. Hawker, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 743-750; cM. A. Tasdelen, Y. Yagci, *Angew. Chem. Int. Ed.* **2013**, *52*, 5930-5938.

[20] C. G. Claessens, U. Hahn, T. Torres, *Chemical Record* **2008**, *8*, 75-97.

10.1002/anie.201912484

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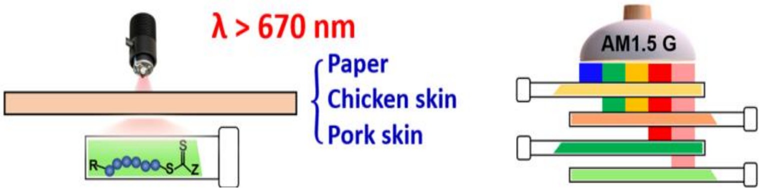

Zilong Wu, Kenward Jung and Cyrille Boyer**

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Effective utilization of NIR wavelengths for photo-controlled polymerization – penetration through thick barriers and parallel solar syntheses

An efficient far-red and NIR light mediated RAFT photopolymerization utilizing phthalocyanines as a photosensitizer is presented. The use of longer wavelengths permits polymerization by irradiating through barriers. Furthermore, long wavelength photochemistry may be used in conjunction with existing photocatalysts to enable more optimized usage of solar irradiation for chemical syntheses.