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**Supporting Information for:** 

## **Recent Advancements in the Development of Molecular Organic Photocatalysts**

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Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	* <i>E<sub>red1/2</sub></i> (V vs SCE)	* <i>E</i> <sub>ox1/2</sub> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\begin{array}{c} E_{ox1/2} \\ \text{(V vs SCE)} \end{array}$	<i>E</i> <sub>00</sub>	Structure				
	Cyanoarenes											
DCB <sup>1-3</sup>	290	9.7	2.55		-1.46		4.01	CN CN CN				
DCA <sup>4-6</sup>	422	14.9	1.99		-0.91		2.90					
4CzIPN <sup>7-16</sup> (MeCN)		12.7	1.43	-1.18	-1.24	1.49	2.67					
3CzClIPN <sup>17</sup> (MeCN)		6.9	1.56	-0.93	-1.16	1.79	2.72					
5CzBN <sup>17</sup> (MeCN)		16.3	1.31	-1.42	-1.52	1.41	2.83	$\begin{array}{c} \begin{array}{c} Cz \\ Cz \\ Cz \\ Cz \end{array} \\ \begin{array}{c} Cz \\ Cz \\ Cz \end{array} \\ \begin{array}{c} Cz \\ Cz \\ Cz \end{array} \\ \begin{array}{c} Cz \\ Cz $				
3DPACIIPN <sup>17</sup> (MeCN)		11.5	1.24	-1.34	-1.41	1.31	2.65					
3DPAFIPN <sup>17</sup> (MeCN)		4.2	1.09	-1.38	-1.59	1.30	2.68	DPA NC DPA F DPA F				
3DPA2FBN <sup>17</sup> (DCM)		4.2	0.92	-1.60	-1.92	1.24	2.84	DPA CN DPA F DPA PA DPA DPA DPA DPA				

Table S1. Available Photophysical and Electrochemical Data for Reviewed PC	s.
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Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	* <i>E<sub>red1/2</sub></i> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\begin{array}{c} E_{ox1/2} \\ \text{(V vs SCE)} \end{array}$	E <sub>00</sub>	Structure
4MeOCzIPN <sup>1</sup> 7 (MeCN/DCM 5:1)			1.27	-1.50	-1.34	1.11	2.61	MeOCz MeOCz MeOCz MeOCz MeOCz MeOCz MeO
5MeOCzBN <sup>17</sup> (MeCN)			1.15	-1.79	-1.66	1.02	2.81	MeOCz MeOCz MeOCz MeOCz MeOCz MeOCz MeOCz
	•			Acridiniun	n		*	
ACR2 <sup>18</sup> Acr <sup>+</sup> -Mes (MeCN)	430	6.4	2.06		-0.57		2.63	
ACR3 <sup>18</sup> (MeCN)	420	14.4	2.08		-0.59		2.67	BF <sub>4</sub>
ACR4 <sup>18</sup> (MeCN)	466	18.7	1.90		-0.57		2.47	MeO BF <sub>4</sub>

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
ACR5 <sup>18</sup> (MeCN)	407	3.0	2.01		-0.71		2.72	
ACR6 <sup>18</sup> (MeCN)	414	1.3	1.65		-0.82		2.47	MeO OMe MEO OME
ACR7 <sup>18</sup> (MeCN)	412	1.3	1.62		-0.84		2.46	MeO Me BF <sub>4</sub> OMe
ACR8 <sup>19, 20</sup> 3-cyano-1- methylquinoli nium perchlorate			2.72					CN CIO <sub>4</sub>
ACR9 <sup>21</sup> (MeCN)	419	16.4	2.11		-0.56		2.67	tBu N TBu

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	$E_{\theta\theta}$	Structure
ACR10 <sup>21</sup> (MeCN)	421	16.8	2.13		-0.54		2.67	tBu BF <sub>4</sub>
ACR11 <sup>21</sup> (MeCN)	427	16.1	2.16		-0.47		2.63	tBu BF <sub>4</sub>
ACR12 <sup>21</sup> (MeCN)	425	17.1	2.21		-0.43		2.64	tBu BF <sub>4</sub>
ACR13 <sup>21</sup> (MeCN)	431	19.0	2.09		-0.53		2.62	tBu N BF <sub>4</sub>
ACR14 <sup>21</sup> (MeCN)	460	0.3	2.07		-0.53		2.60	tBu BF <sub>4</sub>

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
ACR15 <sup>21</sup> (MeCN)	462	0.3	2.06		-0.54		2.60	
ACR16 <sup>21</sup> (MeCN)	422	1.1	2.05		-0.58		2.63	tBu BF4 OMe
ACR17 <sup>21</sup> (MeCN)	419	17.6	2.11		-0.55		2.66	
ACR18 <sup>21</sup> (MeCN)	421	18.4	2.12		-0.54		2.66	tBu BF <sub>4</sub> CO <sub>2</sub> Et
ACR19 <sup>21</sup> (MeCN)	421	20.7	2.14		-0.51		2.65	tBu BF <sub>4</sub> CF <sub>3</sub>

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
ACR20 <sup>21</sup> (MeCN)	425	20.8	2.19		-0.45		2.64	HBU - HBU BF <sub>4</sub> F <sub>3</sub> C CF <sub>3</sub>
ACR21 <sup>21</sup> (MeCN)	419	2.7	2.17		-0.50		2.67	tBu BF <sub>4</sub> N
ACR22 <sup>21</sup> (MeCN)	421	22.8	2.14		-0.53		2.67	
ACR23 <sup>21</sup> (MeCN)	422	23.7	2.13		-0.54		2.67	tBu - tBu BF <sub>4</sub>
ACR24 <sup>21</sup> (MeCN)		25.7	2.20		-0.39		2.59	IBU BU BF <sub>4</sub> IBU

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
N,N'-di-n- propyl-1,13- dimethoxyqui nacridinium (nPr- DMQA+) tetrafluorobor ate <sup>22</sup> (MeCN)	616	5.5	1.15	-0.61	-0.78	1.32	1.93	Pr <sup>n</sup> N Pr <sup>n</sup> BF <sub>4</sub>
				Phenazine	8			
AZ1 N,N'- diphenyl- 5,10- dihydrophena zine <sup>23, 24</sup> (DMA)	369 (0.61)	3	-2.34 (determined by DFT)					
AZ2 5,10-di(4- trifluorometh ylphenyl)- 5,10- dihydrophena zine <sup>23, 25</sup> (DMAc)	367 (0.52)	1-3	-2.24 (calculate in different solvent) -1.74 in DMAc			0.28	2.02	CF <sub>3</sub> CF <sub>3</sub> CF <sub>3</sub> CF <sub>3</sub>

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\begin{array}{c} E_{ox1/2} \\ \text{(V vs SCE)} \end{array}$	$E_{\theta\theta}$	Structure
AZ3 5,10-dihydro- 5,10-bis(4- methoxyphen yl)- phenazine <sup>24</sup>			-2.36 (determined by DFT)					
AZ4 4,4'-(5,10- phenazinediyl )bis- benzonitrile <sup>24</sup>			-2.06 (determined by DFT)					
AZ5 5,10-dihydro- 5,10-di-2- naphthalenyl- phenazine <sup>26, 27</sup> (DMA)	343 (0.60)	4.3 μs	-2.20 (determined by DFT)			0.21	1.90	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	* <i>E<sub>red1/2</sub></i> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\begin{array}{c} E_{ox1/2} \\ (V \text{ vs SCE}) \end{array}$	$E_{\theta\theta}$	Structure
AZ6 5,10-dihydro- 5,10-di-1- naphthalenyl- phenazine <sup>26</sup> (DMA)	362 (0.50)		-2.12 (determined by DFT)					
AZ7 2,3,7,8- tetrabromo- 5,10-di(4- trifluorometh ylphenyl)- 5,10- dihydrophena zine <sup>25</sup> (DMAc)	385 (1.08)					0.60		$ \begin{array}{c}  & CF_{3} \\  & F_{3} \\  & F_{3} \\  & Br_{3} \\  & Br_{3} \\  & F_{3} \\  & $
AZ8 2,3,5,7,8,10- hexakis(4- (trifluorometh yl)phenyl)- 5,10- dihydrophena	385 (1.44)		-1.68			0.45	2.13	$F_{3}C$ $F_{3}C$ $F_{3}C$ $F_{3}C$ $F_{3}C$ $F_{3}C$ $CF_{3}$ $CF_{3}$ $CF_{3}$

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\begin{array}{c} E_{ox1/2} \\ \text{(V vs SCE)} \end{array}$	$E_{\theta\theta}$	Structure
zine <sup>25</sup> (DMAc)								
AZ9 2,3,7,8- tetra([1,1'- biphenyl]-4- yl)-5,10- bis(4- (trifluorometh yl)phenyl)- 5,10- dihydrophena zine <sup>25</sup> (DMAc)	389 (2.22)		-1.86			0.34	2.20	$CF_3$
AZ10 2,3,7,8- tetra(naphthal en-2-yl)-5,10- bis(4- (trifluorometh yl)phenyl)- 5,10- dihydrophena	388 (2.00)		-1.84			0.38	2.22	$ \begin{array}{c}                                     $

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\frac{E_{ox1/2}}{(V \text{ vs SCE})}$	$E_{\theta\theta}$	Structure
zine <sup>25</sup>								
(DMAc)								
AZ11								
2,3,7,8- tetrakis(4- methoxyphen yl)-5,10- bis(4- (trifluorometh yl)phenyl)- 5,10- dihydrophena zine <sup>25</sup> (DMAc)	388 (1.14)		-1.81			0.27	2.08	MeO MeO MeO CF <sub>3</sub> MeO CF <sub>3</sub> OMe
AZ12 4,4',4'',4'''- tetrakis(N,N- dimethylanili ne)-(5,10- bis(4- (trifluorometh yl)phenyl)- 5,10-	392 (1.46)		-1.88			0.15	2.03	CF <sub>3</sub> N N N N CF <sub>3</sub> N N CF <sub>3</sub>

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\frac{E_{ox1/2}}{(V \text{ vs SCE})}$	<i>E</i> <sub>00</sub>	Structure
dihydrophena zine <sup>25</sup>								
(DMAc)								
AZ13								
Benzo[ <i>a</i> ] pyrido[2',1':2,	443							N
3]imidazo[4, 5- <i>c</i> ] phenazine <sup>28, 29</sup>	(0.98)	3.8	-2.17	1.70	-1.45	0.98	3.15	
(CHCl <sub>3</sub> )								
AZ14								
2,3-dimethyl- benzo[ <i>a</i> ] pyrido[2',1':2, 3]imidazo[4, 5- <i>c</i> ] phenazine <sup>28, 29</sup>	443 (1.11)	3.0	-1.63	1.15	-1.47	0.99	2.62	
(CHCl <sub>3</sub> )								

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	$E_{\theta\theta}$	Structure
AZ15 2,3-dichloro- benzo[ $a$ ] pyrido[2',1':2, 3]imidazo[4, 5- $c$ ] phenazine <sup>28, 29</sup> (CHCl <sub>3</sub> )	460 (1.07)	4.5	-1.61	1.29	-1.37	1.05	2.66	
AZ16 2,3-dibromo- benzo[ $a$ ] pyrido[2',1':2, 3]imidazo[4, 5- $c$ ] phenazine <sup>28, 29</sup> (CHCl <sub>3</sub> )	462 (0.83)	1.2	1.15	-1.40	-1.35	1.10	2.50	Br N N
PHEN1 <sup>30</sup> (MeCN)	371			2.73		0.49	-2.24	
PHEN2 <sup>30</sup> (MeCN)	376			2.81		0.74	-2.08	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	$E_{\theta\theta}$	Structure
PHEN3 <sup>30</sup> (MeCN)	420			2.40		0.80	-1.60	
PHEN4 <sup>30</sup> (MeCN)	412			2.43		1.03	-1.39	
PHEN5 <sup>30</sup> (MeCN)	414			2.57		0.26	-2.31	
PHEN6 <sup>30</sup> (MeCN)	412			2.58		0.57	-2.02	
PHEN7 <sup>30</sup> (MeCN)	408			2.57		0.68	-1.89	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
PHEN8 <sup>30</sup> (MeCN)	410			2.56		0.65	-1.91	
PHEN9 <sup>30</sup> (MeCN)	408			2.55		0.76	-1.79	
				Thiazines				-
Methylene Blue <sup>31-34</sup> (MeCN)	664 (9.00)	32 µs	0.97		-0.47		1.50	
Thionin <sup>31, 34-36</sup> (MeCN)	598 (5.80)	20 µs	1.35		-0.34		1.69	H <sub>2</sub> N N
New Methylene Blue N <sup>34</sup> (MeCN)	622 (1.80)	11 µs	1.34		-0.39		1.73	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
1,9-dimethyl Methylene Blue <sup>34</sup> (MeCN)	652 (8.50)	12 µs	1.03		-0.47		1.50	
Methylene Green <sup>34</sup> (MeCN)	654 (6.00)	14 µs	1.28		-0.22		1.50	
Tris-acetyl- PTH <sup>37</sup> (MeCN)	Visible light		-1.50					
PTH (10H- Phenothiazine) <sup>38</sup> (MeCN)			-2.10			0.68		
	1	1	1	Oxazines	1	1		
Nile Blue <sup>34, 39-</sup> 42 (MeCN)	630	1.76	0.87		-1.05		1.92	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
Nile Red <sup>43-45</sup> (MeCN) <sup>46</sup>	543	4.56			-1.02			
Brilliant Cresyl Blue ALD <sup>34</sup> (MeCN)	616 (4.50)	0.51	1.67		-0.31		1.98	0.5 ZnCl <sub>2</sub> Me H <sub>2</sub> N O N(Et) <sub>2</sub>
OX1 <sup>47</sup> (DMAc)	389 (2.40)		-1.72			0.42	2.14	
OX2 <sup>27</sup> (DMA)	388 (2.66)	480± 50 μs	-1.80			0.65	2.45	
OX3 <sup>47</sup> (DMAc)	384 (2.59)		-1.70			0.43	2.13	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	* <i>E<sub>red1/2</sub></i> (V vs SCE)	* <i>E</i> <sub>ox1/2</sub> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	$\begin{array}{c} E_{ox1/2} \\ (V \text{ vs SCE}) \end{array}$	$E_{\theta\theta}$	Structure
OX4 <sup>48</sup> (DMAc)		3.24			-2.70	0.63	3.03	
OX5 <sup>48</sup> (DMAc)	371 (1.50)	6.32			-2.35	0.66	2.79	
OX6 <sup>48</sup> (DMAc)	367 (1.83)	8.03			-2.40	0.64	2.86	
OX7 <sup>47</sup> (DMAc)	362 (1.03)		-1.71			0.53	2.24	
OX8 <sup>47</sup> (DMAc)	363 (2.20)		-1.91			0.37	2.28	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	E <sub>00</sub>	Structure
OX9 <sup>47</sup> (DMAc)	411 (2.23)		-1.42			0.62	2.04	
OX10 <sup>47</sup> (DMAc)	388 (2.11)		-1.58			0.58	2.16	F <sub>3</sub> C
OX11 <sup>47</sup> (DMAc)	384 (2.53)		-1.69			0.40	2.09	
OX12 <sup>47</sup> (DMAc)	355 (1.91)		-1.72			0.46	2.18	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	E <sub>00</sub>	Structure
OX13 <sup>47</sup> (DMAc)	379 (2.06)		-1.85			0.45	2.30	
OX14 <sup>47</sup> (DMAc)	382 (3.77)		-1.88			0.30	2.18	
OX15 <sup>47</sup> (DMAc)	369 (1.08)		-1.60			0.54	2.14	
OX16 <sup>49</sup> (MeCN)	383 (2.70)			-1.98		0.72	2.86	
				Xanthene				

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E</i> <sub>00</sub>	Structure
Fluorescein <sup>50-</sup> <sup>52</sup> (MeOH)	491 (H <sub>2</sub> O)	4.73			-1.22	0.83		Na <sup>-O</sup> , O, O O, Na
Rose Bengal <sup>50, 53</sup> (MeOH)	549	0.50	1.18	-1.33	-0.99	0.84	2.17	
Eosin Y (MeCN)	528 (7.78)	4.1	1.30	-1.53	-1.00	0.77	2.30	Na Br Br O Br O Na
E-ph <sub>3</sub> (MeCN)	550 (4.16)	3.4	1.10	-1.82	-1.11	0.39	2.21	
E- trifluorometh ylph <sub>3</sub> (MeCN)	553 (4.98)		1.20	-1.65	-0.99	0.54	2.19	

Photocatalyst (solvent) <sup>ref</sup>	λ <sub>max,abs</sub> (ε (10 <sup>4</sup> M <sup>-</sup> cm <sup>-</sup> ))	τ <sub>0</sub> (ns)	*E <sub>red1/2</sub> (V vs SCE)	* <i>E<sub>ox1/2</sub></i> (V vs SCE)	<i>E<sub>red1/2</sub></i> (V vs SCE)	<i>E<sub>ox1/2</sub></i> (V vs SCE)	E <sub>00</sub>	Structure
E-tertbutylph <sub>3</sub> (MeCN)	559 (6.01)	2.7	1.14	-1.89	-1.06	0.31	2.20	
E-naph <sub>3</sub> (MeCN)	564 4.88)	3.2	1.12	-1.72	-1.08	0.48	2.20	

## 9. References

- 1. H. D. Roth, T. Herbertz, R. R. Sauers and H. Weng, Intramolecular nucleophilic capture of radical cations by tethered hydroxy functions, *Tetrahedron*, 2006, **62**, 6471-6489.
- 2. D. Mangion, J. Kendall and D. R. Arnold, Photosensitized (electron-transfer) deconjugation of 1arylcyclohexenes, *Organic letters*, 2001, **3**, 45-48.
- 3. K. Ohkubo, K. Suga, K. Morikawa and S. Fukuzumi, Selective oxygenation of ring-substituted toluenes with electron-donating and-withdrawing substituents by molecular oxygen via photoinduced electron transfer, *Journal of the American Chemical Society*, 2003, **125**, 12850-12859.
- 4. F. D. Lewis, R. E. Dykstra, I. R. Gould and S. Farid, Cage escape yields and direct observation of intermediates in photoinduced electron-transfer reactions of cis-and trans-stilbene, *J. Phys. Chem.*, 1988, **92**, 7042-7043.
- 5. Y. Wang, O. Haze, J. P. Dinnocenzo, S. Farid, R. S. Farid and I. R. Gould, Bonded exciplexes. A new concept in photochemical reactions, *The Journal of organic chemistry*, 2007, **72**, 6970-6981.
- 6. I. R. Gould, D. Ege, J. E. Moser and S. Farid, Efficiencies of photoinduced electron-transfer reactions: role of the Marcus inverted region in return electron transfer within geminate radical-ion pairs, *Journal of the American Chemical Society*, 1990, **112**, 4290-4301.
- 7. F. Lima, L. Grunenberg, H. B. Rahman, R. Labes, J. Sedelmeier and S. V. Ley, Organic photocatalysis for the radical couplings of boronic acid derivatives in batch and flow, *Chem. Commun.*, 2018, **54**, 5606-5609.
- 8. S. He, X. Chen, F. Zeng, P. Lu, Y. Peng, L. Qu and B. Yu, Visible-light-promoted oxidative decarboxylation of arylacetic acids in air: Metal-free synthesis of aldehydes and ketones at room temperature, *Chinese Chemical Letters*, 2019.
- 9. Z. Huang, Y. Gu, X. Liu, L. Zhang, Z. Cheng and X. Zhu, Metal-Free Atom Transfer Radical Polymerization of Methyl Methacrylate with ppm Level of Organic Photocatalyst, *Macromol. Rapid Commun.*, 2017, **38**, 1600461.
- 10. H. Jiang and A. Studer, Transition-Metal-Free Three-Component Radical 1, 2-Amidoalkynylation of Unactivated Alkenes, *Chemistry–A European Journal*, 2019, **25**, 516-520.
- 11. Z.-Y. Song, C.-L. Zhang and S. Ye, Visible light promoted coupling of alkynyl bromides and Hantzsch esters for the synthesis of internal alkynes, *Org. Biomol. Chem.*, 2019, **17**, 181-185.
- 12. T.-Y. Shang, L.-H. Lu, Z. Cao, Y. Liu, W.-M. He and B. Yu, Recent advances of 1, 2, 3, 5-tetrakis (carbazol-9-yl)-4, 6-dicyanobenzene (4CzIPN) in photocatalytic transformations, *Chem. Commun.*, 2019, **55**, 5408-5419.
- T. Ju, Q. Fu, J. H. Ye, Z. Zhang, L. L. Liao, S. S. Yan, X. Y. Tian, S. P. Luo, J. Li and D. G. Yu, Selective and Catalytic Hydrocarboxylation of Enamides and Imines with CO2 to Generate α, α-Disubstituted α-Amino Acids, *Angew. Chem. Int. Ed.*, 2018, **57**, 13897-13901.
- 14. N. R. Patel, C. B. Kelly, A. P. Siegenfeld and G. A. Molander, Mild, redox-neutral alkylation of imines enabled by an organic photocatalyst, *ACS Catal.*, 2017, **7**, 1766-1770.
- 15. J. Santandrea, C. Minozzi, C. Cruché and S. K. Collins, Photochemical Dual-Catalytic Synthesis of Alkynyl Sulfides, *Angew. Chem. Int. Ed.*, 2017, **56**, 12255-12259.
- 16. T. C. Sherwood, H.-Y. Xiao, R. G. Bhaskar, E. M. Simmons, S. Zaretsky, M. P. Rauch, R. R. Knowles and T. M. Dhar, Decarboxylative intramolecular arene alkylation using N-(acyloxy) phthalimides, an organic photocatalyst, and visible light, *J. Org. Chem.*, 2019, **84**, 8360-8379.
- 17. E. Speckmeier, T. G. Fischer and K. Zeitler, A toolbox approach to construct broadly applicable metal-free catalysts for photoredox chemistry: deliberate tuning of redox potentials and

importance of halogens in donor–acceptor cyanoarenes, J. Am. Chem. Soc., 2018, **140**, 15353-15365.

- A. Joshi-Pangu, Levesque, F., Roth, H. G., Oliver, S. F., Campeau, L., Nicewicz, D., DiRocco, D. A., Acridinium-Based Photocatalysts: A Sustainable Option in Photoredox Catalyst, *J. Org. Chem.*, 2016, **81**, 7244-7249.
- 19. K. Ohkubo, T. Kobayashi and S. Fukuzumi, Direct oxygenation of benzene to phenol using quinolinium ions as homogeneous photocatalysts, *Angew. Chem. Int. Ed.*, 2011, **50**, 8652-8655.
- 20. D. A. Nicewicz, Nguyen, T. M., Recent Applications of Organic Dyes as Photoredox Catalyst in Organic Synthesis, *ACS Catalysis*, 2013, 355-360.
- 21. A. R. White, L. Wang and D. A. Nicewicz, Synthesis and Characterization of Acridinium Dyes for Photoredox Catalysis, *Synlett*, 2019, **30**, 827-832.
- 22. L. Mei, J. M. Veleta and T. L. Gianetti, Helical Carbenium Ion: A Versatile Organic Photoredox Catalyst for Red-Light-Mediated Reactions, *J. Am. Chem. Soc.*, 2020, **142**, 12056-12061.
- 23. D. Koyama, H. J. Dale and A. J. Orr-Ewing, Ultrafast observation of a photoredox reaction mechanism: photoinitiation in organocatalyzed atom-transfer radical polymerization, *J. Am. Chem. Soc.*, 2018, **140**, 1285-1293.
- 24. J. C. Theriot, C.-H. Lim, H. Yang, M. D. Ryan, C. B. Musgrave and G. M. Miyake, Organocatalyzed atom transfer radical polymerization driven by visible light, *Science*, 2016, **352**, 1082-1086.
- 25. J. P. Cole, C. R. Federico, C.-H. Lim and G. M. Miyake, Photoinduced organocatalyzed atom transfer radical polymerization using low ppm catalyst loading, *Macromolecules*, 2019, **52**, 747-754.
- 26. C.-H. Lim, M. D. Ryan, B. G. McCarthy, J. C. Theriot, S. M. Sartor, N. H. Damrauer, C. B. Musgrave and G. M. Miyake, Intramolecular charge transfer and ion pairing in N, N-diaryl dihydrophenazine photoredox catalysts for efficient organocatalyzed atom transfer radical polymerization, *Journal of the American Chemical Society*, 2017, **139**, 348-355.
- 27. Y. Du, R. M. Pearson, C. H. Lim, S. M. Sartor, M. D. Ryan, H. Yang, N. H. Damrauer and G. M. Miyake, Strongly reducing, visible-light organic photoredox catalysts as sustainable alternatives to precious metals, *Chemistry–A European Journal*, 2017, **23**, 10962-10968.
- K. Podemska, R. Podsiadły, A. M. Szymczak and J. Sokołowska, Diazobenzo [a] fluorene derivatives as visible photosensitizers for free radical polymerization, *Dyes and Pigments*, 2012, 94, 113-119.
- 29. K. Podemska, R. Podsiadly, A. Orzel and J. Sokołowska, The photochemical behavior of benzo [a] pyrido [2', 1': 2, 3] imidazo [4, 5-c] phenazine dyes, *Dyes and Pigments*, 2013, **99**, 666-672.
- 30. D. Liu, M.-J. Jiao, Z.-T. Feng, X.-Z. Wang, G.-Q. Xu and P.-F. Xu, Design, Synthesis, and Application of Highly Reducing Organic Visible-Light Photocatalysts, *Org. Lett.*, 2018, **20**, 5700-5704.
- 31. H.-J. Timpe and S. Neuenfeld, Photoreduction of some dyes by styrene, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2329-2336.
- 32. T. Ohno and N. N. Lichtin, Electron transfer in the quenching of triplet methylene blue by complexes of iron (II), *J. Am. Chem. Soc.*, 1980, **102**, 4636-4643.
- R. Kayser and R. Young, The photoreduction of methylene blue by amines—I. A flash photolysis study of the reaction between triplet methylene blue and amines, *Photochem. Photobiol.*, 1976, 24, 395-401.
- 34. S. P. Pitre, C. D. McTiernan and J. C. Scaiano, Library of cationic organic dyes for visible-lightdriven photoredox transformations, *ACS Omega*, 2016, **1**, 66-76.
- 35. U. Steiner, G. Winter and H. E. Kramer, Investigation of physical triplet quenching by electron donors, *J. Phys. Chem.*, 1977, **81**, 1104-1110.
- 36. H. Fischer, H. E. Kramer and A. Maute, Blitzlichtuntersuchungen über die ausbleichreaktion von thionin mit allylthioharnstoff, II, *Z. Phys. Chem.*, 1970, **69**, 113-131.

- 37. S. O. Poelma, G. L. Burnett, E. H. Discekici, K. M. Mattson, N. J. Treat, Y. Luo, Z. M. Hudson, S. L. Shankel, P. G. Clark and J. W. Kramer, Chemoselective radical dehalogenation and C–C bond formation on aryl halide substrates using organic photoredox catalysts, *J. Org. Chem.*, 2016, **81**, 7155-7160.
- E. H. Discekici, N. J. Treat, S. O. Poelma, K. M. Mattson, Z. M. Hudson, Y. Luo, C. J. Hawker and J. R. de Alaniz, A highly reducing metal-free photoredox catalyst: design and application in radical dehalogenations, *Chemical Communications*, 2015, **51**, 11705-11708.
- 39. C.-W. Lin, J. R. Shulok, S. D. Kirley, L. Cincotta and J. W. Foley, Lysosomal localization and mechanism of uptake of Nile blue photosensitizers in tumor cells, *Cancer research*, 1991, **51**, 2710-2719.
- 40. S. Daehne, U. Resch-Genger and O. S. Wolfbeis, *Near-infrared dyes for high technology applications*, Springer Science & Business Media, 2012.
- 41. J. L. Smith, On the simultaneous staining of neutral fat and fatty acid by oxazine dyes, *J Pathol Bacteriol*, 1908, **12**, 4.
- 42. J. Jose and K. Burgess, Benzophenoxazine-based fluorescent dyes for labeling biomolecules, *Tetrahedron*, 2006, **62**, 11021-11037.
- 43. P. Greenspan, E. P. Mayer and S. D. Fowler, Nile red: a selective fluorescent stain for intracellular lipid droplets, *J. Cell Biol.*, 1985, **100**, 965-973.
- 44. M. Neumann, S. Füldner, B. König and K. Zeitler, Metal-free, cooperative asymmetric organophotoredox catalysis with visible light, *Angew. Chem. Int. Ed.*, 2011, **50**, 951-954.
- 45. A. Kawski, B. Kukliński and P. Bojarski, Photophysical properties and thermochromic shifts of electronic spectra of Nile Red in selected solvents. Excited states dipole moments, *Chemical Physics*, 2009, **359**, 58-64.
- 46. J. Xu, S. Shanmugam, H. T. Duong and C. Boyer, Organo-photocatalysts for photoinduced electron transfer-reversible addition–fragmentation chain transfer (PET-RAFT) polymerization, *Polymer Chemistry*, 2015, **6**, 5615-5624.
- 47. B. G. McCarthy, R. M. Pearson, C.-H. Lim, S. M. Sartor, N. H. Damrauer and G. M. Miyake, Structure–property relationships for tailoring phenoxazines as reducing photoredox catalysts, *Journal of the American Chemical Society*, 2018, **140**, 5088-5101.
- 48. S. M. Sartor, Y. M. Lattke, B. G. McCarthy, G. M. Miyake and N. H. Damrauer, Effects of Naphthyl Connectivity on the Photophysics of Compact Organic Charge-Transfer Photoredox Catalysts, *J. Phys. Chem. A*, 2019, **123**, 4727-4736.
- 49. D. S. Lee, C. S. Kim, N. Iqbal, G. S. Park, K.-s. Son and E. J. Cho, Organophotocatalytic Arene Functionalization: C–C and C–B Bond Formation, *Org. Lett.*, 2019.
- 50. T. Shen, Z.-G. Zhao, Q. Yu and H.-J. Xu, Photosensitized reduction of benzil by heteroatomcontaining anthracene dyes, *Journal of Photochemistry and Photobiology A: Chemistry*, 1989, **47**, 203-212.
- 51. X. F. Zhang, I. Zhang and L. Liu, Photophysics of halogenated fluoresceins: involvement of both intramolecular electron transfer and heavy atom effect in the deactivation of excited states, *Photochemistry and photobiology*, 2010, **86**, 492-498.
- 52. M. M. Martin and L. Lindqvist, The pH dependence of fluorescein fluorescence, *Journal of Luminescence*, 1975, **10**, 381-390.
- 53. K. Fidaly, C. Ceballos, A. Falguières, M. S.-I. Veitia, A. Guy and C. Ferroud, Visible light photoredox organocatalysis: a fully transition metal-free direct asymmetric α-alkylation of aldehydes, *Green Chemistry*, 2012, **14**, 1293-1297.