Electronic Supplementary Information (ESI)

Development of Rare-earth-free Organic Phosphors for Eco-energy Lighting Based LEDs

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A. Reaction between Synthesis of 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile and aliphatic amines

General procedure: all products were prepared according to reference.[24]A mixture of (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile, aliphatic amines (**1a-1d**), in acetonitrile was heated under reflux until completion (TLC monitoring). After cooling down to room temperature, the solutions were concentrated under pressure then filtered and washed several times with ethanol. The crude solids were purified by crystallization to give products **(Table 3)**.

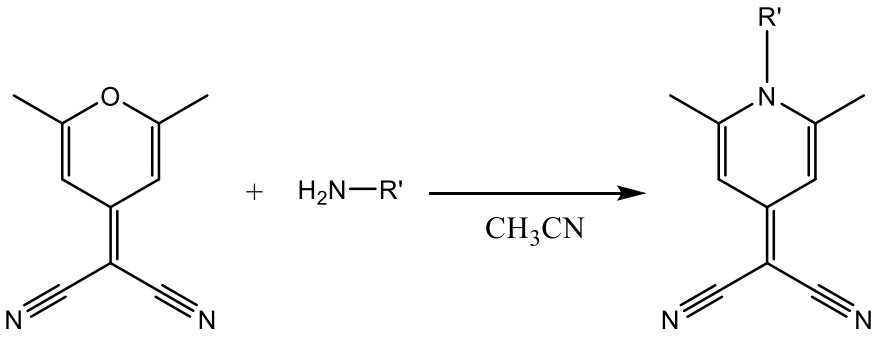
*Synthesis of 2-(1,2,6-trimethylpyridin-4H-ylidene)malonitrile (**2a**)*: (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol), methylamine (1mmol), acetonitrile (50 mL); Purification by crystallization gave **2a** as a white solid: yield (64%). mp >300°C (from acetonitrile). ν_{max}/cm^{-1} 2186(C≡N), 2157, 1633 (C=C), 1558, 1496, 1430, 1359, 1201, 1068, 847, 536. δ_H(400 MHz; DMSO-d_6) 6.64 (s, 2H), 3.58 (s, 3H, CH_3), 2.43 (s, 6H, CH_3). δ_C(100 MHz; DMSO-d_6) 160.4, 150.3, 119.1, 112.1, 77.71, 36.5, 20.5. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{12}N_3$ 186.1031, found 186.1025.

*Synthesis of 2-(1-butyl-2,6-dimethylpyridin-4H-ylidene)malonitrile (**2b**)* : (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol), butylamine (1mmol), acetonitrile (50 mL); Purification by crystallization gave **2b** as a pale-yellow solid: yield (83%). mp 208.6-209.5°C (from acetonitrile). ν_{max}/cm^{-1} 2956, 2868 (CH_2, CH_3), 2190 (C≡N), 2165, 1633 (C=C), 1554, 1504, 1480, 1363, 1342, 1226, 1184, 1068, 844. δ_H(400 MHz; $CDCl_3$) 6.61 (s, 2H), 3.92 (t, *J* = 8.4 Hz, 2H, CH_2), 2.47 (s, 6H, CH_3), 1.76-1.62 (m, 2H, CH_2), 1.64-1.38 (m, 2H, CH_2), 1.01 (t, *J* = 7.4 Hz, 3H, CH_3). δ_C(100 MHz; $CDCl_3$) 155.5, 147.7, 118.8, 113.6, 48.8, 44.0, 31.4, 20.4, 19.8, 13.4. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}N_3$ 228.1501, found 228.1499.

*Synthesis of 2-(1-hexyl-2,6-dimethylpyridin-4H-ylidene)malonitrile (**2c**)* : (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol), hexylamine (1mmol), acetonitrile (50 mL); Purification by crystallization gave **2c** as a white solid: yield (80%) mp 170.2-171.1°C (from acetonitrile). ν_{max}/cm^{-1} 2951, 2926 (CH_2, CH_3), 2186 (C≡N), 2165, 1633 (C=C), 1550, 1496, 1363, 1184, 1064, 839, 540. δ_H(400 MHz; $CDCl_3$) 6.63 (s, 2H), 3.91 (t, *J* = 8.4 Hz, 2H, CH_2), 2.47 (s, 6H, CH_3), 1.75-1.64 (m, 2H, CH_2), 1.47-1.29 (m, 6H, CH_2 chain), 0.92 (t, *J* = 7.2 Hz, 3H, CH_3). δ_C(100 MHz; $CDCl_3$) 155.6, 147.6, 118.8, 113.7, 49.1, 31.0, 29.4, 26.2, 22.3, 20.5, 13.7. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{22}N_3$ 256.1814, found 256.1802.

*Synthesis of 2-(1-octyl-2,6-dimethylpyridin-4H-ylidene)malonitrile (**2d**)* : (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol), octylamine (1mmol), acetonitrile (50 mL); Purification by crystallization gave **2d** as a white solid: yield (64%). mp 155.8-157.1°C (from acetonitrile). ν_{max}/cm^{-1} 2918, 2856 (CH_2, CH_3), 2190 (C≡N), 2170, 1625 (C=C), 1546, 1508, 1484, 1380, 1351, 1313, 1184, 1068, 873, 536. δ_H(400 MHz; $CDCl_3$) 6.63 (s, 2H), 3.91 (t, *J* = 8.3 Hz, 2H, CH_2), 2.47 (s, 6H, CH_3), 1.74-1.64 (br, 2H, CH_2), 1.44-1.17 (br, 10H, CH_2 chain), 0.89 (t, *J* = 7.0 Hz, 3H, CH_3). δ_C(100 MHz; $CDCl_3$) 155.6, 147.6, 118.8, 113.7, 49.1, 44.2, 31.5, 29.5, 28.8, 26.5, 22.4, 20.5, 13.9. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{26}N_3$ 284.2127, found 284.2127.

Table S1. Reactions of (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile with various aliphatic amines



1a -1d **2a -2d**

Entry	Aliphatic amine (R'-NH_2)	Product	Yield (%)
1a	methylamine, CH_3NH_2 (n=1)	2a	64
1b	butylamine, $CH_3(CH_2)_3NH_2$ (n=4)	2b	83
1c	hexylamine, $CH_3(CH_2)_5NH_2$ (n=6)	2c	80
1d	octylamine, $CH_3(CH_2)_7NH_2$ (n=8)	2d	64

B. Reaction between Synthesis of 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile andaromatic aldehydes

General procedure: all products were prepared according to reference.[23, 40] A mixture of (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile, aromatic aldehydes (**3a-3e**), and piperidine in acetonitrile was heated under reflux until completion (TLC monitoring). After cooling down to room temperature, the precipitate solids was filtered and washed several times with cold methanol. The crude solids were purified by crystallization to give products **(Table 4)**.

*Synthesis of 2-(2,6-distyryl-4H-pyran-4'-ylidene)malononitrile (**4a**)*: (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol); benzaldehyde (2mmol); piperidine (2mmol); acetonitrile (50 mL); Purification by crystallization gave **4a** as a red solid: yield (44%). mp 252.9-253.4°C (from acetonitrile/dichloromethane). ν_{max}/cm^{-1} 2207 (C≡N), 1642 (C=C), 1608, 1541, 1500, 1417, 1330, 1304, 1197, 1180, 972, 943, 831, 756, 697, 481. δ_H(400 MHz; $CDCl_3$) 7.63-7.58 (dd, 3H, Ar, *J* = 7.5, 1.65 Hz), 7.56 (d, *J* = 16.1 Hz, 2H, trans C=C), 7.50-7.43 (m, 6H, Ar), 6.79 (d, *J* = 16.1 Hz, 2H, trans C=C), 6.72 (s, 2H). δ_C(100 MHz; $CDCl_3$) 158.4, 156.1, 138.4, 134.8, 130.8, 129.5, 128.1, 118.8, 115.4, 107.6. MS (ESI) m/z: $[M]^+$ calcd for $C_{24}H_{16}N_2O$ 348.1263, found xxx.

*Synthesis of 2-(2,6-bis(2-naphthalen-2-yl)vinyl)-4H-pyran-4'-ylidene)malononitrile (**4b**)*: (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol); 2-naphthaldehyde (2mmol); piperidine (2mmol); acetonitrile (50 mL); Purification by crystallization gave **4b** as an orange solid: yield (43%). mp 268.7-268.6°C (from toluene). ν_{max}/cm^{-1} 2207 (C≡N), 1643 (C=C), 1542, 1498, 1418, 1172, 955, 854, 810, 741, 472. δ_H(400 MHz; $CDCl_3$; the signal of TFA was not included) 8.06 (s, 2H, Ar), 7.96-7.86 (m, 6H, Ar), 7.78 (d, *J* = 16 Hz, 2H, trans C=C), 7.78 (d, *J* = 1.6 Hz, 2H, Ar), 7.61-7.55 (m, 4H, Ar), 6.94 (d, *J* = 16.1 Hz, 2H, trans C=C), 6.81 (s, 2H). δ_C(100 MHz; $CDCl_3$; the signal of TFA was not included) 190.9, 159.2, 138.9, 134.4, 133.4, 131.9, 130.1, 129.1, 128.6, 128.2, 127.9, 127.7, 127.1, 123.1, 118.4, 107.3, 57.4. MS (ESI) m/z: $[M]^+$ calcd for $C_{32}H_{20}N_2O$ 448.1576, found xxx.

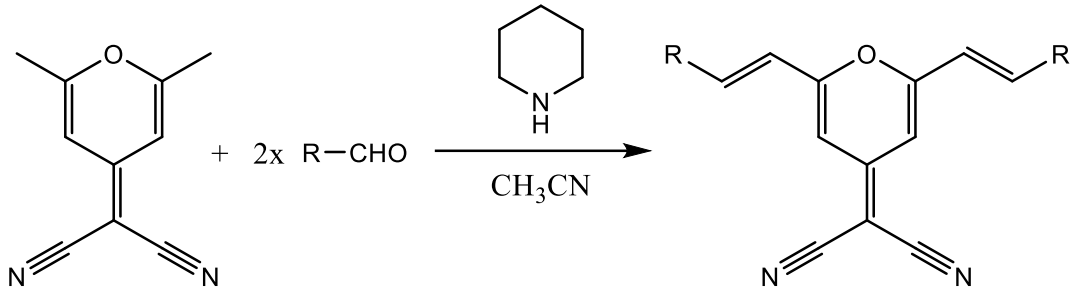
*Synthesis of 2-(2,6-bis(2-(anthracen-9-yl)vinyl)-4H-pyran-4'-ylidene)malononitrile (**4c**)*: (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol); anthracene-9-carboxaldehyde (2mmol); piperidine (2mmol); acetonitrile (50 mL); Purification by crystallization gave **4c** as a red powder: yield (48%). mp >300°C (from toluene). ν_{max}/cm^{-1} 2207 (C≡N), 1643 (C=C), 1503, 1420, 1254, 1189, 949, 877, 842, 723, 546. δ_H(400 MHz; $CDCl_3$; the signal of TFA was not included) 8.79 (d, *J* = 16.3 Hz, 2H, trans C=C), 8.54 (s, 2H, Ar), 8.36 (d, *J* = 8.6 Hz, 4H, Ar), 8.08 (d, *J* = 8.3 Hz, 4H, Ar), 7.63-7.51 (m, *J* = 6.9 Hz, 8H, Ar), 7.00 (d, J = 16 Hz, 2H, trans C=C), 6.98 (s, 2H). δ_C(100 MHz; $CDCl_3$; the signal of TFA was not included) 197.3, 161.96, 131.4, 129.3, 127.1, 125.6, 124.7, 118.4, 115.6, 112.8, 109.9, 108.0, 59.5. MS (ESI) m/z: $[M]^+$ calcd for $C_{40}H_{24}N_2O$ 548.1889, found xxx.

*Synthesis of 2-(2,6-bis(2-(pyridin-3-yl)vinyl)-4H-pyran-4'-ylidene)malononitrile (**4d**)*: (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol); 3-pyridinecarboxaldehyde (2mmol); piperidine (2mmol); acetonitrile (50 mL); Purification by crystallization gave **4d** as a yellow powder: yield (53%). mp >300°C (from toluene). ν_{max}/cm^{-1} 2207 (C≡N), 1646 (C=C), 1542, 1498, 1415, 1302, 1206, 1023, 972, 946, 833, 795, 700. δ_H(400 MHz; $CDCl_3$; the signal of TFA was not included) 9.13 (s, 2H, Ar), 8.82 (d, *J* = 5.7 Hz, 2H, Ar), 8.21-8.10 (br, 2H, Ar), 7.78 (d, *J* = 16.1 Hz, 2H, trans C=C), 7.30 (d, *J* = 16.3 Hz, 2H, trans C=C), 7.15 (s, 2H). δ_C(100 MHz; $CDCl_3$; the signal of TFA was not included) 179.6, 157.7, 144.3, 141.3, 140.9, 136.0, 130.0, 128.2, 126.2, 113.0, 110.7, 61.2. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{15}N_4O$ 351.1246, found 351.1274.

*Synthesis of 2-(2,6-bis(4-(methoxystyryl)-4H-pyran-4'-ylidene)malononitrile (**4e**)*: (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile (1mmol); 4-methoxybenzaldehyde (2mmol); piperidine (2mmol); acetonitrile (50 mL); Purification by crystallization gave **4e** as an orange solid: yield (58%). mp 236.0-238.2°C (from toluene). ν_{max}/cm^{-1} 2207 (C≡N), 1640 (C=C), 1605, 1536, 1492, 1418, 1302, 1261, 1172, 1029, 964, 827, 507. δ_H(400 MHz; $CDCl_3$; the signal of TFA was not included): 7.56 (d, J = 8.4 Hz, 2H, Ar), 7.53 (d, *J* = 15.2 Hz, 2H, trans C=C), 6.98 (d, *J*

= 8.8 Hz, 2H, Ar), 6.71 (s, 2H), 6.67 (d, J = 16.1 Hz, 2H, trans C=C). 2207 (C≡N), 1640 (C=C), 1605, 1536, 1492, 1418, 1302, 1261, 1172, 1029, 964, 827, 507. δ_C(100 MHz; $CDCl_3$; the signal of TFA was not included) 161.6, 159.5, 157.4, 138.4, 129.7, 127.3, 115.9, 114.7, 113.0, 106.5, 56.2, 55.5. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{20}N_2O_3$ 408.1474, found xxx.

Table S2. Reactions of (2,6-dimethyl-4H-pyran-4'-ylidene)malononitrile with various aromatic aldehydes



3a -3e **4a -4e**

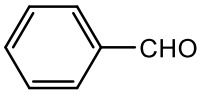
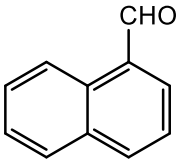
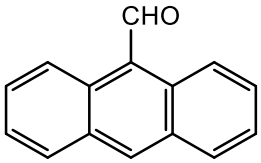
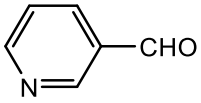
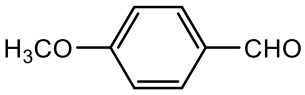
Entry	Aromatic aldehyde (R-CHO)	Product	Yield (%)
3a		4a	44
3b		4b	43
3c		4c	48
3d		4d	53
3e		4e	58

Figure S3. Synthesis of methyl pyrazinylketone benzoyl hydrazone (**5a**) and its complex(**5b**)