Supplementary Materials

Details of color quantification

Color perception is a complex human activity involving physical, physiological and psychological counterparts[1]. This sensation arises from brain activity in response to signals received via the optic nerve from the eye and from the anatomical perspective this phenomenon is the primary function of photoreceptors built in human eyes[2]. The tristimulus factors are the quantities of three primary contributions to the additive color model, sufficient to match any perceived color[3]. Many mathematical formulations were proposed for quantification of color perception[4] and so called CIE XYZ or CIE Lab standards[5] are ones of common usage. These standards are based on a numerical description of the chromatic response of an observer to optical stimulus. However, due to the distribution of cones in the eye, the tristimulus values depend on the observation angle. To eliminate this variable, the CIE defined the colorimetric standard of the observer assuming that color-sensitive cones reside within 2° arc of the fovea. Thus, the XYZ tristimulus values represent the reflectance or transmittance spectrum weighted by color-matching functions and integrated over the whole spectrum. The visible spectrum is then sufficient for XYZ tristimulus values prediction. Unfortunately, many disadvantages of such definition were pointed out[6] and so called CIE Lab Standard[3,7] has been proposed in 1976 for measuring color and its differences. It defines new parameters, L, a, b, representing psychometric lightness, red-green and yellow-blue axes, respectively. The color-matching functions represent normalized cone cell response under photopic conditions at medium and high level of illumination. The color-matching functions, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ characterize the amount of XYZ tristimulus (where X=red, Y=green and Z=blue). For actual calculation of tristimulus values XYZ it is necessary to take into account both illuminant spectral power P(λ) and transmittance of transparent media T(λ), (or reflectance in case of opaque materials) according to the following formula:

$$X(\lambda) = k \sum_{\lambda=360}^{830} P(\lambda) \cdot T(\lambda) \cdot \bar{x}(\lambda) \quad \text{(S1)}$$

$$Y(\lambda) = k \sum_{\lambda=360}^{830} P(\lambda) \cdot T(\lambda) \cdot \bar{y}(\lambda) \quad \text{(S2)}$$

$$Z(\lambda) = k \sum_{\lambda=360}^{830} P(\lambda) \cdot T(\lambda) \cdot \bar{z}(\lambda) \quad \text{(S3)}$$

$$k = \frac{100}{Y(\lambda)} \quad \text{(S4)}$$

The integrated tristimulus values X, Y and Z define the color of These so called CIE Lab parameters are directly related to XYZ tristimulus as follows:

$$L^* = 116(Y/Y_n)^{1/3} - 16, \quad if\ Y/Y_n > 0.008856 \quad \text{(S5)}$$

$$L^* = 116(Y/Y_n)^{1/3} - 16, \quad if\ Y/Y_n > 0.008856 \quad \text{(S6)}$$

$$a^* = 500[f(X/X_n) - f(Y/Y_n)] \quad \text{(S7)}$$

$$b^* = 200[f(Y/Y_n) - f(Z/Z_n)] \quad \text{(S8)}$$

$$f(I) = 7.787 \cdot I + 16/116, \quad if\ I > 0.008856 \quad \text{(S9)}$$

$$f(I) = I^3, \qquad if\ I > 0.008856 \quad \text{(S10)}$$

where X_n, Y_n and Z_n are the tristimulus values of a specified reference white color and are equivalent to the illuminant itself if computed for the perfect reflecting diffuser.

References

1. C. H. Graham, *Vision and visual perception*, Wiley, New York, 1965.
2. L. M. Hurvich and D. Jameson, *Psychol. Rev.*, 1957, **64**, 384.
3. R. W. Hunt, *Measuring colour* (3rd ed.). Fountain Press, England, 1998.
4. S. Westland and C. Ripamonti, *Computational Colour Science, using MATLAB*, Wiley, Chichester, UK, 2004.
5. J. Schanda, *Colorimetry. Understanding the CIE system*, Wiley, 2007.
6. A. D.Broadbent, *Color Res. Appl.*, 2004, **29**, 267.
7. A. N. Netravali and B. G. Haskell, *Digital Pictures: Representation, Compression, and Standards* (2nd ed.), Springer, 1986.

Table S1 Results of color prediction by broad range of electron density functionals using 6-31G(d,p) basis set both for geometry optimization and electronic spectrum computations. The values provided in the first column represent mean color differences estimated based on eq.3 with respect to experimental value for the whole set of six concentrations of AZ in methanol.

ΔE	**λ_{max} [nm]**	f	**Acronym**	**DFT functional**
2.5	**430.2**	**0.151**	**HSE2PBE**	Known also as HSE03, Heyd-Scuseria-Ernzerhof hybrid functional[s1]
2.7	**431.7**	**0.150**	**HSEh1PBE**	Known also as HSE06, full Heyd-Scuseria-Ernzerhof hybrid[s1]
2.9	**433.0**	**0.150**	**B972**	Becke's B97[s2] functional modified by Wilson, Bradley and Tozer[s3]
3.0	**433.4**	**0.148**	**B98**	Version of Becke's functional from 1998[s4]
3.2	**434.0**	**0.146**	**X3LYP**	Hybrid functional with LYP correction to exchange energy introduced by Xu and Goddard[s5]
3.5	**424.2**	**0.156**	**PBE0**	Known also as PBE1PBE, the 1996 pure functional of Perdew, Burke and Ernzerhof[s6], as made into a hybrid by Adamo[s7]
4.0	**422.5**	**0.157**	**PBEh1PBE**	Hybrid using the 1998 revised form of PBE pure exchange and correlation functional[s8]
4.3	**421.7**	**0.158**	**mPW1PW91**	Hybrid functional using modified by Adamo and Barone Perdew-Wang exchange and PW91 correlation[s9]
4.4	**437.5**	**0.146**	**B971**	Handy, Tozer and coworkers modification to B97[s10]
4.6	**420.8**	**0.152**	**B1LYP**	Becke's one parameter hybrid functional[s11] with Lee–Yang–Parr (LYP) correlation functional[s12] introduced by Adamo and Barone[s13]
4.7	**420.3**	**0.146**	**mPW1PBE**	Hybrid functional with1996 gradient-corrected correlation functional of Perdew, Burke and Ernzerhof (PBE)[s6] and modified by Adamo and Barone Perdew-Wang one parameters (mPW1)[s9]
5.8	417.1	0.154	M06	The hybrid functional of Zhao and Truhlar[s14]
6.0	441.1	0.143	B3LYP	Becke's three parameter hybrid functional with LYP correlation functional[s15]
6.3	441.8	0.147	B3PW91	Becke's three parameter hybrid functional with the non-local PW91 correlation[s15]
6.4	442.1	0.148	B3P86	Becke's three parameter hybrid functional with 1986 Perdew (P86) nonlocal correlation[s15]
6.5	414.6	0.157	B1B95	One parameter hybrid functional using Becke's corrections to exchange and correlation energies[s11]
6.6	442.4	0.148	mPW3PBE	Hybrid functional with PBE gradient-corrected correlation functional and Perdew-Wang exchange modified by Adamo and Barone[s9]
17.6	463.1	0.136	τHCTHhyb	Handy's hybrid τ-dependent gradient-corrected correlation functional[s16]
21.1	375.0	0.186	BMK	Boese and Martin's τ-dependent hybrid functional[s17]
21.8	372.8	0.208	CAM-B3LYP	Long range corrected version of B3LYP applying the Coulomb-attenuating method[s18]
22.6	473.3	0.131	O3LYP	A three-parameter functional similar to B3LYP[s19]
22.7	473.6	0.131	TPSSh	The τ-dependent gradient-corrected functional introduced by Tao, Perdew, Staroverov, and Scuseria[s20]
24.3	362.0	0.214	ωB97X-D	Head-Gordon dispersion interaction corrected functional[s21]
25.3	353.7	0.197	M06-2X	The hybrid functional of Truhlar and Zhao[s22]
25.5	351.4	0.209	BHandH	Half-and-half type of functional which include LYP correlation, half Hartree-Fock exchange and half LSDA (Local Spin Density Approximation) exchange [s15]
25.8	344.5	0.200	BHandHLYP	Half-and-half type of functional which include Becke's 1988 and LSDA exchange, LYP correlation functional and Hartree-Fock correction to exchange energy[s15]
26.1	335.0	0.241	ωB97X	Long range corrected hybrid functional from Head-Gordon which includes dispersion contribution[s23]
26.2	324.4	0.257	LC-ωPBE	Long range-corrected version of ωPBE[s24]
26.2	322.8	0.252	ωB97	Long range corrected hybrid functional from Head-Gordon which includes dispersion contribution[s23]
26.3	295.6	0.247	M06-HF	The hybrid functional introduced by Truhlar and Zhao[s25]
26.3	421.0	0.152	mPW1LYP	Hybrid combining LYP correlation energy correction[s12] and modified by Adamo and Barone Perdew-Wang one parameter (mPW1) exchange functional[s9]
28.4	487.4	0.121	M06-L	The pure functional of Truhlar and Zhao[s26]
29.0	567.0	0.109	S	The Slater Exchange functional also referred to as Local Spin Density exchange[s27]
30.6	554.4	0.100	B	Becke's 1988 functional, combining Slater exchange with corrections involving density gradient[s28]
30.9	552.9	0.112	Xα	Standalone exchange functional[s27]
32.5	502.2	0.109	VSXC	τ-Dependent gradient-corrected correlation functional of van Voorhis and Scuseria[s29]
33.3	534.9	0.107	B97D	Grimme's functional including dispersion[s30]
33.4	533.5	0.111	τHCTH	Handy's hybrid τ-dependent gradient-corrected correlation functional[s16]
33.5	532.4	0.110	HCTH147	One of the Handy's functionals including gradient-corrected correlation[s10,s31]
33.7	530.9	0.110	HCTH93	One of the Handy's functionals including gradient-corrected correlation[s10,s31]
33.8	529.5	0.111	HCTH	One of the Handy's functionals including gradient-corrected correlation[s10,s31]
33.8	529.5	0.111	HCTH407	One of the Handy's functionals including gradient-corrected correlation[s10,s31]

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s1. (a) J. Heyd and G. Scuseria, *J. Chem. Phys.*, 2004, **121**, 1187. (b) J. Heyd and G. E. Scuseria, *J. Chem. Phys.*, 2004, **120**, 7274. (c) J. Heyd, J. E. Peralta, G. E. Scuseria, and R. L. Martin, *J. Chem. Phys.*, 2005, **123**, 174101. (d) J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.*, 2006, **124**, 219906. (e) A. F. Izmaylov, G. Scuseria, and M. J. Frisch, *J. Chem. Phys.*, 2006, **125**, 104103. (f) A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106. (g) T. M. Henderson, A. F. Izmaylov, G. Scalmani, and G. E. Scuseria, *J. Chem. Phys.*, 2009, **131**, 044108.

s2. A. D. Becke, *J. Chem. Phys.*, 1997, **107**, 8554.

s3. P. J. Wilson, T. J. Bradley, and D. J. Tozer, *J. Chem. Phys.*, 2001, **115**, 9233.

s4. H. L. Schmider and A. D. Becke, *J. Chem. Phys.*, 1998, **108**, 9624.

s5. X. Xu and W. A. Goddard III, *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 2673.

s6. (a) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865. (b) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

s7. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

s8. M. Ernzerhof and J. P. Perdew, *J. Chem. Phys.*, 1998, **109**, 3313.

s9. C. Adamo and V. Barone, *J. Chem. Phys.*, 1998, **108**, 664.

s10. F. A. Hamprecht, A. Cohen, D. J. Tozer, and N. C. Handy, *J. Chem. Phys.*, 1998, **109**, 6264.

s11. A. D. Becke, *J. Chem. Phys.*, 1996, **104**, 1040.

s12. (a) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785. (b) B. Miehlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.

s13. C. Adamo and V. Barone, *Chem. Phys. Lett.*, 1997, **274**, 242.

s14. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

s15. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648. (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.

s16. A. D. Boese and N. C. Handy, *J. Chem. Phys.*, 2002, **116**, 9559.

s17. A. D. Boese and J. M. L. Martin, *J. Chem. Phys.*, 2004, **121**, 3405.

s18. T. Yanai, D. Tew, and N. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.

s19. A. J. Cohen and N. C. Handy, *Mol. Phys.*, 2001, **99**, 607.

s20. J. M. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.

s21. J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.

s22 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

s23. J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106.

s24. (a) Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, *J. Chem. Phys.*, 2004, **120**, 8425. (b) O. A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 234109. (c) O. A. Vydrov, J. Heyd, A. Krukau, and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 074106. (d) O. A. Vydrov, G. E. Scuseria, and J. P. Perdew, *J. Chem. Phys.*, 2007, **126**, 154109.

s25 (a) Y. Zhao and D. G. Truhlar, *J. Phys. Chem.*, 2006, **110**, 5121. (b) Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 13126.

s26. Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.

s27. (a) P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864-B71. (b) W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140** A1133-A38. (c) J. C. Slater, *The Self-Consistent Field for Molecular and Solids, Quantum Theory of Molecular and Solids, Vol. 4*, McGraw-Hill, New York, 1974.

s28. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

s29. T. Van Voorhis and G. E. Scuseria, *J. Chem. Phys.*, 1998, **109**, 400.

s30. S. Grimme, *J. Comp. Chem.*, 2006, **27**, 1787.

s31. (a) A. D. Boese, N. L. Doltsinis, N. C. Handy, and M. Sprik, *J. Chem. Phys.*, 2000, **112**, 1670. (b) A. D. Boese and N. C. Handy, *J. Chem. Phys.*, 2001, **114**, 5497.

Table S2 Structural formulas of all Alizarin isomers including rotameric and tautomeric forms. Both the relative energy with respect to the most stable isomer and percentage content of the isomer at room temperature (estimated using the Boltzmann distribution) are shown in parenthesis.

(0.0 kcal/mol**; 86.2%)**

(1.5 kcal/mol**; 13.8%)**

(5.4 kcal/mol**; <0.01%)**

(8.2 kcal/mol; 0.0%)

(20.0 kcal/mol; 0.0%)

(18.3 kcal/mol; 0.00%)

VII (23.5 kcal/mol; 0.0%)

VIII (25.8 kcal/mol; 0.0%)

(31.4 kcal/mol; 0.0%)

(13.6 kcal/mol; 0.0%)

(17.2 kcal/mol; 0.0%)

(30.6 kcal/mol; 0.0%)

(23.0 kcal/mol; 0.0%)

(13.8 kcal/mol; 0.0%)

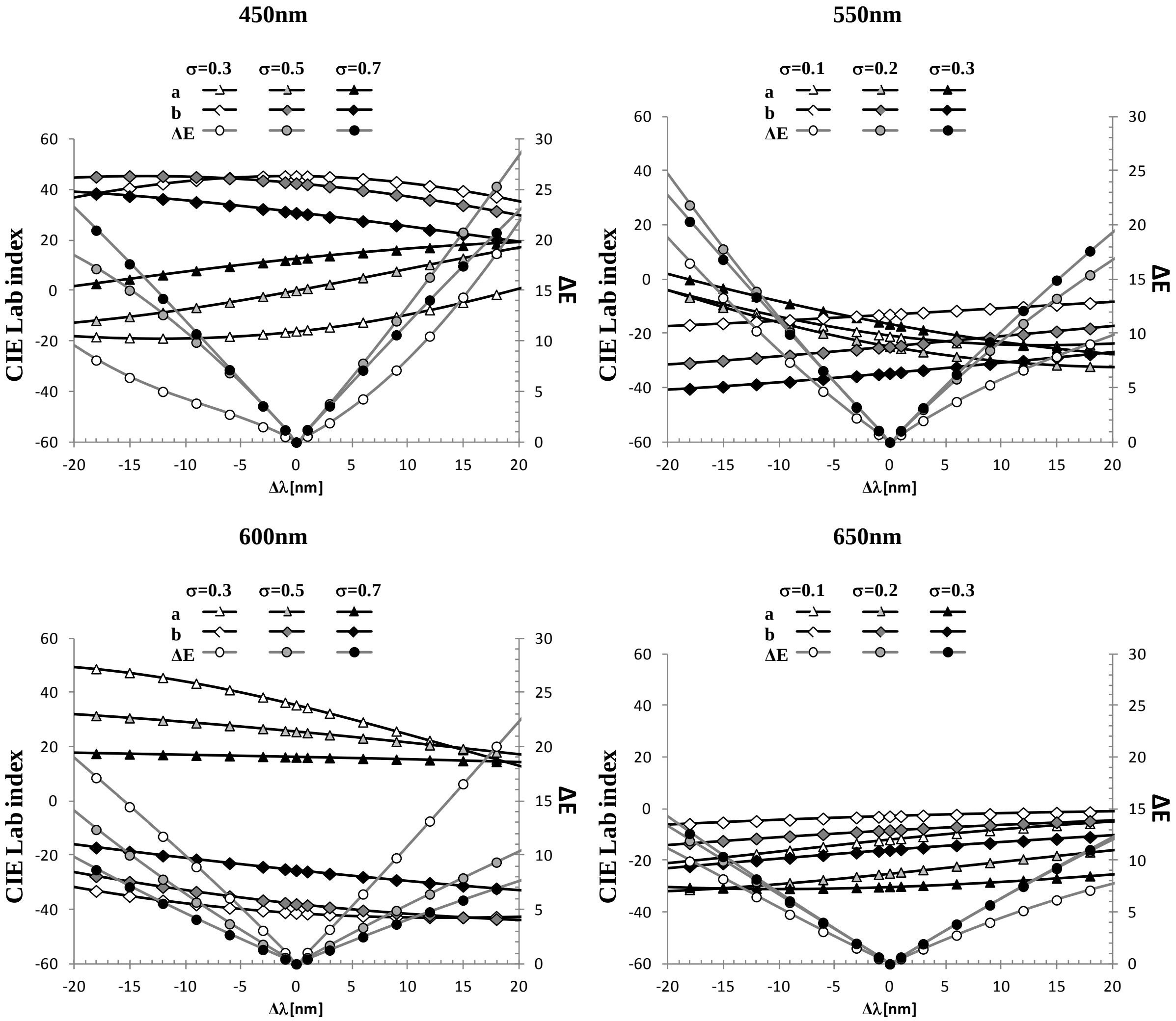

Fig. S1 The color dependence on the two parameters of SBA model, namely Δλ=error in λ_{max}, and σ half band width, expressed as variations of CIEa and CIEb parameters, as well as associated color change ΔE. The normalization condition fixes values of the oscillator strength to f=$\sigma \cdot 2\sqrt{\ln 2/\pi}$.